FUNCTIONALIZING THREE-DIMENSIONAL SUPERHYDROPHOBIC MATERIALS

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University of Massachusetts Amherst

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https://doi.org/10.7275/32753295 https://scholarworks.umass.edu/dissertations_2/2753

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FUNCTIONALIZING THREE-DIMENSIONAL SUPERHYDROPHOBIC MATERIALS

A Dissertation Presented
By
Li He

Submitted to the Graduate School of
the University of Massachusetts Amherst in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY
February 2023
Department of Civil and Environmental Engineering
FUNCTIONALIZING THREE-DIMENSIONAL SUPERHYDROPHOBIC MATERIALS

A Dissertation Presented

by

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ACKNOWLEDGEMENTS

My sincerest gratitude first goes to my advisor, Prof. Guoping Zhang, who has always been supporting me over the past years. His professional guidance and generous help, and encouragement throughout my 4-year study. I am extremely thankful for not only his enlightening on my academic path but also the advice about how to become a person with good citizenship, which encourages me to grow in the future. I am also thankful to Prof. Liu and Prof. Chen for providing help with my experiments. Their generosity to offer help and expertise in mechanics inspire me and provide a lot of insights into my research. I would also like to extend my gratitude to my committee members, Prof. Gerasimidis and Prof. Westgate for their valuable advice on my dissertation.

This research was generously funded by the Berger Award Winner and Charles F. Perrel Scholarship. Additional support from the Graduate School Return to Research Grant, and Geosynthetic Institute Fellowship Grant were also gratefully acknowledged.

I would like to thank all my past and present fellow students for their help and advice throughout my research.

Finally, I would also like to my husband (Pengchao Hu), my parents (Guohong He and Qiongying Fu), and my whole family for their continuous support and understanding when undertaking my research and writing my project. Their love and encouragement for me were what sustained me this far.
ABSTRACT

FUNCTIONALIZING THREE-DIMENSIONAL SUPERHYDROPHOBIC MATERIALS

FEBRUARY 2023

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Traditional bulk superhydrophobic materials are usually characterized by high porosity, low fracture toughness, and extremely low strength due to the low surface energy on the internal surface. Therefore, it is very challenging to achieve a bulk superhydrophobic material with high strength and mechanical durability. This dissertation presents an experimental study of strengthening a superhydrophobic siloxane using carbon-based nanomaterials, emphasizes the effects of microscale dispersion and macroscale distribution of reinforcing graphene on the uniformity and strength of the composite, studies the impact factors on the water adsorption for hydrophilic and hydrophobic materials, and applies chemical modification modify the surface of clay and sands.

Carbon-based nanomaterials are ideal materials to reinforce the pure bulk superhydrophobic materials. The water contact angles of all new synthesized carbon-based reinforcements of superhydrophobic polymers are greater than 150°, and the surface energies are less than 1 mJ/m². The mechanical durability can be indicated by the nanoindentation technique, unconfined compression, and wear testing. Young’s modulus can achieve up to 7 GPa and 5.7 MPa at the micro, and macro-scale, respectively. The mechanisms of reinforcements include carbon-based nanomaterials as nanomaterials fill the pores and bridge the fracture, physically being tangled with aluminosilicones after breaking C-C bonds with the help of the ultrasonic wave and chemical reactions with functional groups.

To study and improve uniform dispersion and distribution of graphene nanoplatelets, three different processing methods were adopted: (1) ultrasonication to disperse graphene in the sol; (2)
accelerated co-condensation at elevated temperature (i.e., 50°C and 75°C) to prevent graphene from floating; (3) varying the soil’s viscosity to control graphene’s flotation. Adding only 0.9 wt.% graphene results in highly strengthened superhydrophobic composites with macroscopic compression strengths of up to ~33MPa. However, graphene tends to float upward in the sol, leading to its heterogeneous distribution within the cured samples. On the other hand, despite its functionality of improving microscale dispersion, ultrasonication also detrimentally decreases the composites’ strength due to acoustic cavitation-induced porosity. Similarly, although high-temperature curing accelerates the condensation of the precursor sol and hence results in a more uniform distribution of graphene, it also promotes thermal cavitation and bubble formation.

To analyze the difference in isothermal adsorption between hydrophilic and hydrophobic materials, the alkali activation of metakaolin by using materials with different functional groups was synthesized. The biggest difference between the isothermal curves of hydrophilic and hydrophobic is the shape, and also there are several factors to influence the adsorption: surface morphology, surface wettability, the size of pore diameter, and specific surface area.

In addition, inspired by the sol-gel method with different functional groups, modification clay and sands with other surfactants can also be hydrophobic materials, the largest water contact angle is 146.9 ± 0.4°. The surface roughness and size of pore diameter are vital to achieving a high-water contact angle. Due to their hydrophobic properties, the modified clay and sands are promising to be used in geotechnical and transportation engineering.

**KEYWORDS:** Alkali activation; Carbon-based nanomaterials; Cavitation; Isothermal adsorption; Nanoindentation; Organosilanes; Sol-gel; Surface hierarchical; Superhydrophobicity, Ultrasonic wave.
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<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$\gamma_{SL}$</td>
<td>Solid-liquid surface tension</td>
<td>dynes/cm</td>
</tr>
<tr>
<td>$\gamma_{LV}$</td>
<td>Liquid-vapor surface tension</td>
<td>dynes/cm</td>
</tr>
<tr>
<td>$\gamma_{SV}$</td>
<td>Solid-vapor surface tension</td>
<td>dynes/cm</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Water contact angle</td>
<td>°</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>Apparent contact angle</td>
<td>°</td>
</tr>
<tr>
<td>$r$</td>
<td>Surface roughness factor</td>
<td>–</td>
</tr>
<tr>
<td>$f_s$</td>
<td>Area fraction of the liquid droplet in contact with the solid surface</td>
<td>–</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus</td>
<td>GPa</td>
</tr>
<tr>
<td>$H$</td>
<td>Hardness</td>
<td>GPa</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of X-ray</td>
<td>Å</td>
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<tr>
<td>$P$</td>
<td>Indentation load</td>
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</tr>
<tr>
<td>$h_c$</td>
<td>Contact depth</td>
<td>nm</td>
</tr>
<tr>
<td>$h_f$</td>
<td>Final unloading depth</td>
<td>nm</td>
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<td>$m$</td>
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<td>$\varepsilon$</td>
<td>Geometric constant for the indenter</td>
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<tr>
<td>$E_r$</td>
<td>Reduced elastic modulus</td>
<td>GPa</td>
</tr>
</tbody>
</table>
$E_i$ Young’s modulus of the indenter GPa

$\nu$ Poisson’s ratio for the samples –

$\nu_i$ Poisson’s ratio of the indenter –

$\gamma_{lp}$ the liquid polar components mJ/m$^2$

$\gamma_{ld}$ the liquid dispersive components mJ/m$^2$

$\gamma_{sd}$ the solid dispersive components mJ/m$^2$

$\gamma_{sp}$ the solid polar components mJ/m$^2$

$\gamma_s$ surface energy mJ/m$^2$

$R_g$ the radius of gyration nm
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Explanation</th>
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<tr>
<td>APS</td>
<td>Advanced Photo Source</td>
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<tr>
<td>APTMS</td>
<td>3-Aminopropytrimethoxysilane</td>
</tr>
<tr>
<td>APTS</td>
<td>3-Amino-propyl-trimethoxysilane</td>
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<tr>
<td>BDDT</td>
<td>Brunauer-Deming-Deming-Teller</td>
</tr>
<tr>
<td>BSEs</td>
<td>Backscattered Electrons</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BJH</td>
<td>Barret-Joyner-Halenda</td>
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<td>CNTs</td>
<td>Carbon Nanotubes</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<tr>
<td>CSM</td>
<td>Continuous Stiffness Measurement</td>
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<tr>
<td>DIM</td>
<td>Diiodomethane</td>
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<tr>
<td>DMDCS</td>
<td>Dimethyldichlorosilane</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
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<tr>
<td>FAS</td>
<td>Fluoro-alkyl-silane</td>
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<tr>
<td>FHH</td>
<td>Frenkel-Halsey</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>HFTS</td>
<td>Heptadeca-fluoro-decyltri-chlorosilane</td>
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<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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<tr>
<td>LBL</td>
<td>Layer-by-layer</td>
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<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
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<tr>
<td>MK</td>
<td>Metakaolnin</td>
</tr>
<tr>
<td>MPS</td>
<td>Methacryloxypro-Pyltrimethoxysilane</td>
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<tr>
<td>MTMS</td>
<td>Methyltrimethoxysilane</td>
</tr>
<tr>
<td>MWNTs</td>
<td>Multi-wall Nanotubes</td>
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<tr>
<td>NA</td>
<td>Nitrogen Adsorption</td>
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<tr>
<td>NIL</td>
<td>Nano-imprint Lithography</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source</td>
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<tr>
<td>PDA</td>
<td>Poly-dopamine</td>
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<tr>
<td>PDMS</td>
<td>Poly-dimethyl-siloxane</td>
</tr>
<tr>
<td>POSS</td>
<td>Polyhedral Oligomeric Silsesquioxane</td>
</tr>
<tr>
<td>PTMS</td>
<td>Phenyl-tri-methoxysilane</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SEs</td>
<td>Secondary Low-energy Electrons</td>
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<tr>
<td>SHOIP</td>
<td>Superhydrophobic Hybrid Organic-inorganic Polymer</td>
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<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
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<tr>
<td>SWNTs</td>
<td>Single-wall Nanotubes</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethyl Silane</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>USAXS</td>
<td>Ultra-small-angle X-ray Scattering</td>
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<tr>
<td>VETs</td>
<td>Vapor Equilibrium Techniques</td>
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<tr>
<td>WCA</td>
<td>Water contact angle</td>
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<tr>
<td>RH</td>
<td>Relative Humidity</td>
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<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
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<tr>
<td>SWCC</td>
<td>Soil-Water-Characteristic Curve</td>
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CHAPTER

1. INTRODUCTION

1.1 BACKGROUND

Surface wettability is essential to scientific research and industrial technologies. The wettability of a solid’s surface is influenced by its chemical compositions and physical structure or roughness (L. Zhang et al., 2014). A general way to describe wettability characteristics of a surface is the contact angle of water droplets resting on the surface. The contact angle of water is the angle between the liquid-solid interface and the tangent line of the curve at the contact point of solid, liquid, and gas (Figure 1.1). The wetting behavior of a surface is basically determined by the relation of the interfacial energies between the solid and liquid ($\gamma_{SL}$), between the substrate and the gaseous atmosphere/vapor ($\gamma_{SV}$), and between the liquid and the gaseous atmosphere ($\gamma_{LV}$) (Otitoju et al., 2017). The relationship between these quantities and the contact angle of a droplet on the surface is described by the Young’s equation (Equation 1.1).

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$ (1.1)

where $\theta$ is the contact angle, and $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$ are the interfacial energy at the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively.

Based on the Young’s equation, a surface can be categorized as hydrophilic, hydrophobic, super-hydrophilic, and superhydrophobic surface with water contact angle. When a water contact

Figure 1.1: Contact angle ($\theta$); $\gamma_{LV}$: liquid-vapor surface tension; $\gamma_{SV}$: solid-vapor surface tension; $\gamma_{SL}$: solid-liquid surface tension (Otitoju et al., 2017).
angle $\theta$ is greater than 90°, then the surface is hydrophobic; otherwise, it is hydrophilic. A surface with a water contact angle of greater than 150° is defined or classified as superhydrophobic (Figure 1.2).

![Figure 1.2 surface wettability: (a): $\theta < 90^\circ$ Hydrophilic surface; (b): $\theta > 90^\circ$ Hydrophobic surface; (c): $\theta > 150^\circ$ Superhydrophobic surface (V. Anand Ganesh, 2011).](image)

It is now well accepted that micro-topography or multiscale hierarchical roughness plays an important role in the wettability or contact angle of a solid surface. The normal way to fabricate superhydrophobic surfaces is to create rough structures with hydrophobic components (Drelich et al., 2011). There are two possible cases of a solid surface’s wetting that may occur, which were proposed a long time ago by Wenzel and Cassie-Baxter. Based on the Wenzel model, for a rough surface, it has a higher actual surface area than a smooth surface, and the liquid droplets form to contact with the entire surface and completely penetrate the cavities on the rough surface. For such a rough surface the “apparent” contact angle $\theta_a$ for a liquid droplet is related to the contact angle of the droplet on a smooth surface by the roughness factor $r$ of the surface as described in Equation 1.2.

$$
cos\theta_a = r \cos\theta
$$

(1.2)

where the surface roughness factor $r$ is defined as the ratio of the total surface area to the projected area (Equation 1.3) (Banerjee et al., 2015).

$$
r = \frac{\text{Total Surface Area}}{\text{Projected Area}}
$$

(1.3)

The Wenzel equation suggests that the hydrophobicity of a surface depends on the nature of the corresponding surface. For a hydrophobic surface (i.e., $\theta > 90^\circ$ and $r > 1$), a surface’s hydrophobicity increases with increasing the surface roughness factor $r$ However, the Wenzel
model is not enough to deal with all heterogeneous surfaces. In this case, another model, the Cassie-Baxter model, assumes that a liquid droplet cannot completely penetrate the surface cavities, which suggests that the spreading of a liquid droplet on a surface invalidates the solid-vapor interface and forms combined solid-liquid and liquid-vapor interfaces as shown in Figure 1.3. According to the Cassie-Baxter model, the “apparent” contact angle $\theta_a$ for a liquid droplet on a rough surface is related to the contact angle by Equation 1.4.

$$\cos \theta_a = -1 + f_s (\cos \theta + 1)$$

Where, $f_s$ means the area fraction of the liquid droplet in contact with the solid surface ($f_s < 1$).

It is easy to find various types of hydrophobic and superhydrophobic surfaces in nature. For plants, such as a lotus leaf, shows superhydrophobicity with low adhesion with the solid surface. For insects, various insect wings exhibit superhydrophobic properties, and water striders have remarkable non-wetting legs that enable them to stand effortlessly and move quickly on water surfaces (Xuefeng & Lei, 2004). Using scanning electronic microscopy (SEM) observes the surfaces of plants and insect wings, which revealed hierarchical surface features with numerous microscales or nanoscales roughness (Figure 1.4) (M. Liu et al., 2017). Therefore, it is the most effective way to study nature and then learn the mechanisms of superhydrophobicity in biological organisms. All these nature’s examples show that micro-and nanoscale hierarchical structures have an important role in determining superhydrophobic property. Inspired by nature, it is feasible to make superhydrophobic materials to increase the roughness with hydrophobic components.
Figure 1. Biological surfaces with superhydrophobicity and their multiscale structures: a) lotus leaf; b) cicada wing; c) and e) are SEM images of lotus leaf with different magnifications; d) and f) are SEM images of cicada wing with different magnifications (M. Liu et al., 2017).

Superhydrophobic surfaces and materials can be widely used in practical applications, including self-cleaning, anti-icing, anti-fogging, heat transfer, sensors, energy conversion devices, water-oil separation, and so on. For self-cleaning, the self-cleaning surface prevents or reduces the accumulation of contaminants such as water droplets, dust, stains, and organic matter, which washes away the surface contaminants with the help of gravity (Figure 1.5) (Ganesh et al., 2011). Icing and frosting normally cause lots of troubles in daily life and economic activities which have a long-term impact on human beings. Anti-icing means preventing the accumulation of ice by modifying surface morphology or by low surface energy chemical modification (Parvate et al., 2020). For anti-fogging, collection of fog over surfaces may cause detrimental side effects such as inferior optical properties, the irregular supply of electrical and telecommunication systems, humidity, convection, and conversion into dense ice layer (Howarter & Youngblood, 2008). Anti-fogging coatings can approach the issues of fogging over surfaces and handle a wide range of environmental challenges. The way to anti-fogging is that using a superhydrophobic coating to enhance attractive forces between the surface and discrete fog particulates, which weaken surface tension and disperse condensate droplets to form a continuous, invisible water layer, inducing a
decreased scattering phenomenon and preservation of optical transparency (Chemin et al., 2018). For oil-water separation, because materials have extremely different affinities toward water and oils, when a surface is superhydrophobic to water but superoleophilic to oils, the oil can penetrate the surface, but the water just is remained, so it is an effective way to separate oil and water (Gong et al., 2017).

![Figure 1.5 Lotusan self-cleaning paint (Ganesh et al., 2011).](image)

Superhydrophobic materials (superhydrophobic hybrid organic-inorganic polymers, SHOIP) have been synthesized by our group. In order to improve the properties of superhydrophobic bulk materials and even get the smart surfaces, we try to figure out adding nanoparticles (carbon-based nanoparticles) to enhance the synthesized materials. Therefore, the aim of the proposed research is to extend the application of superhydrophobic bulk materials and enhance their properties. Also, we aim to get smart surfaces that can switch from hydrophilic or superhydrophilic to hydrophobic or superhydrophobic materials. Functionalizing superhydrophobic membranes and coatings have been widely used in our daily life, but there is little research to study functionalized three-dimensional (3D) superhydrophobic materials.
1.2 RESEARCH OBJECTIVES

The aim of this dissertation was to synthesize the functionalized three-dimensional (3D) superhydrophobic materials and study the mechanisms of condensation, strengthen, dispersion, and distribution. After characterization of the synthesized materials, exploring the application of functionalizing 3D superhydrophobic materials for practical, and also extending the method to modify the clay and sand. Specific research objectives are as follows:

- Synthesizing the functionalized superhydrophobic bulk materials and studying the strengthen mechanisms for carbon-based nanoparticles.
- Studying the reinforcement of superhydrophobic siloxane with graphene nanoplatelets and emphasizing the effects of microscale dispersion and macroscale distribution of reinforcing graphene on the uniformity and strength of the composite.
- Analyzing the isothermal adsorption of hydrophilic and hydrophobic materials and distinguishing the difference between materials with different surface wettability.
- Modification surface of clay and sands with the functional groups to achieve the better properties and extend the applications.

1.3 DISSERTATION ORGANIZATION

The dissertation consists of seven chapters and is formatted as a series of standalone papers. A brief outline of each chapter is given below:

(1) Chapter 1 (current chapter) is an introduction to this research, including the background, research objectives, and dissertation organization.
(2) Chapter 2 summarizes a comprehensive review of the synthesis routes for functionalized superhydrophobic materials and their application, and of the carbon-based nanomaterials and their application.
(3) Chapter 3 presents carbon-based reinforcements of superhydrophobic polymers, focuses on the mechanisms of strengthening and the improved strength.
(4) Chapter 4 presents the reinforcement a superhydrophobic material with graphene nanoplatelets and emphasizes the effects of microscale dispersion and macroscale distribution of reinforcing graphene on the uniformity and strength of the composite.

(5) Chapter 5 shows the isothermal adsorption for hydrophilic and hydrophobic materials, distinguishes the difference, and studies the influence factors for the isotherm adsorption.

(6) Chapter 6 presents surface modification for sand and clay with dimethyldichlorosilane under different phases conditions and explores the similarities and difference between different conditions and methods.

(7) Chapter 7 is a conclusion chapter that concludes the significant findings of this dissertation research and provides recommendations for future research on the functionalizing 3D superhydrophobic materials and the synthesis of methods.
2. LITERATURE REVIEW

2.1 INTRODUCTION

The section presents a comprehensive overview of the related literature conducted in the area of functionalized superwetting materials. First, the literature review begins with how to synthesize functionalized superhydrophobic surfaces. Second, the literature review introduces graphene, its exceptional properties, and the applications by combining it with hydrophobic or superhydrophobic materials. Third, introducing the properties of graphene oxide and reduced graphene oxide, and using them how to functionalize the superwetting materials. Finally, a comprehensive overview of the properties, and applications of carbon nanotubes (CNTs) to functionalize the surface of superwetting materials. The literature review should be able to provide a solid background of this proposed research and further cover the insufficient knowledge of the region.

2.2 FUNCTIONALIZING SUPERHYDROPHOBIC SURFACES

2.2.1 Introduction

Superhydrophobic surfaces gradually gain more attention due to their potential applications in multi-fields, such as fluid transportation, environmental protections, bioscience, and so on. Because of the rapid development in the fields of nanotechnology, functionalized superhydrophobic surfaces can be synthesized by adding micro and nano-scale particles, which improves the properties and widens the potential applications of superhydrophobic surfaces. Also, chemical functionalization using some stabilizers, such as organic molecules and polymers, can enhance the properties of superhydrophobic materials (Uddin et al., 2013). By functionalizing the surfaces of superhydrophobic materials and studying the mechanism of condensation, it is hopeful to achieve a smart surface that can be switched from hydrophilic or superhydrophilic to hydrophobic or superhydrophobic surfaces (Lahann et al., 2003) (Figure 2.1).
Figure 2.1 Idealized representation of the transition between straight (hydrophilic) and bent (hydrophobic) molecular conformations (ions and solvent molecules are not shown) (Lahann et al., 2003).

2.2.2 Synthesis Routes of Functionalizing Superhydrophobic Surfaces

Synthetic functionalized superhydrophobic surfaces are being made to harness advanced properties of superhydrophobic materials, where surface chemistry and morphology are tailored to keep the air at the material-water interface (Figure 2.2). Materials used to fabricate superhydrophobic surfaces have intrinsically low surface energy because of non-polar chemistries (i.e., CH₂/CH₃ or CF₂/CF₃) and close-packed, resulting in high water contact angles (> 120°), and roughing surfaces is also very vital to improve the superhydrophobic property. These low-energy materials can be coated onto an already rough material, named “bottom-up” fabrication methods, or be directly processed to result in roughness, termed “top-down” methods, and another way to fabricate superhydrophobic surfaces is the combination of bottom-up with top-down approaches.
The bottom-up method refers to the creation of larger, more complex objects by integrating smaller particles or components. The method in nanofabrication normally includes self-assembly and self-organization. The bottom-up method includes chemical deposition, assemblies of colloids, layer-by-layer methods, sol-gel, electro-spraying, and so on (Block et al., 2017).

Chemical vapor deposition (CVD) is a technique where the gaseous reactant can be deposited onto a substrate to form a non-volatile solid film. The film morphology is mostly determined by the surface morphology of the substrate, which is usually used as a template. But different morphologies can be recognized on the substrate by the selection of the gaseous reactants and change the reaction conditions. CVD is an efficient way to deal with building micro/nanoparticles, nanorods into ordered macroscopic structures. Superhydrophobic films were fabricated by using tetramethylsilane (TMS) and fluoro-alkyl silane (FAS) with microwave plasma-enhanced CVD, which controlled the gas pressure and substrate temperature to determine the surface roughness precisely at levels from 9.4 nm to 60.8 nm (Takai 1997). Superhydrophobic surfaces have been made with two dry process techniques, the first one is nanotexturing with an oxygen plasma treatment, and subsequently hydrophobic coating utilizing low temperature CVD or plasma-enhanced CVD (Teshima et al., 2005).

Self-assembly and layer-by-layer (LBL) methods are the bottom-up approaches for coating surfaces which include the individual molecules that template themselves on the surface to form a dense monolayer. Self-assembled single layers may functionalize a surface to make it hydrophobic or hydrophilic. Self-assembly and LBL are simple and efficient ways to build superhydrophobic surface structures. By changing the size and ratio of the dual-sized particles without
organic/inorganic templates, the desirable micro-nano hierarchical structure for superhydrophobicity was fabricated with self-assembly of dual-sized silica particles from a mixed dispersion (Xu & Wang, 2010). The electrostatic charge interactions as shown in various layers such as polyanion and polycation are based on the LBL deposition. LBL technique is easy, and it determines the thickness of the layer with very high molecular precision. The simple and efficient method for creating the highly transparent superhydrophobic surface with the successive dip coating of 3-amino-propyl-trimethoxysilane (APTS) functionalized silica nanoparticles having two different sizes (100 and 20 nm) (X. Li et al., 2010).

The sol-gel technique can produce highly ordered structures with well-defined chemistry shown particular promise in fabricating superhydrophobic surfaces. The sol-gel procedure is well-realized for synthesizing gels and nanoparticles (as shown in Figure 2.3). The sol-gel approach has been produced for the production of multi-layered films, porous pillars, thin films, nano-crystalline materials, nano-powders, rough coatings with clusters for paints, anti-septics, nanocomposites, drugs, biomedical implants, and military components. The surface roughness getting from the sol-gel method can be easily done by changing the protocol of the method and the arrangement of the reaction mixture. The roughness or pore size of the sol-gel network is determined by the sol-gel kinetics reaction, pH of the reaction medium catalyst used (Y. K. Chen et al., 2009), such as hydrochloric acid, sodium hydroxide, the chemical structure of precursor (Latthe et al., 2010), the molecular weight of the additives and curing temperature (Chang et al., 2008). Superhydrophobic silica coatings was dip-coated on glass substrates with phenyl-tri-methoxy silane (PTMS) and methyl-tri-methoxysilane as a co-precursor with two-step sol-gel process at room temperature (K. Gupta et al., 2015).
The top-down method is an overall term when it comes to the fabrication of materials and devices by carving, molding, or machining bulk materials with tools and lasers in microelectronics, such as lithography, template-based techniques, and surface plasma treatment (K. Gupta et al., 2015).

Lithography is a good way to fabricate large proportions and periodic micro and nano-patterns, especially electronic beam lithography, light lithography, X-ray lithography, and nanospheres lithography. Various types of surface preparation by lithography include when a design is transferred from a master onto a substrate surface, allowing multiple copies to be made. A small pattern to be fabricated for the newly established nano-imprint lithography (NIL) by the approaches which are similar to the original approach of the term contains contact between an inked stamp and the substrate, with micrometer-size features. The superhydrophobic nanopillars (50 nm in diameter and 100 nm in height) were made up with the NIL method by introducing a low surface energy thin film of mono-glycidyl ether-terminated poly-dimethy-lsiloane (PDMS) (Kim et al., 2007). For photolithography, the photoactive polymer layer is irradiated over a mask shadowed through developing stages and leaving a positive or negative image of the mask upon the surface, and it removes exposed or unexposed polymer. Photolithography may be divided into different categories according to the radiation used: UV, X-ray, e beam, and so on. Also, it can utilize a laser or particle beam to etch the surface straightly or expose a photoresist layer, but this
way is a little slow. The pattern surface can be used as a mask for deposition or etching directly on the substrate. Lithography is useful for fabricating superhydrophobic surfaces for the well-defined shape of the features and the pattern.

Template-based technology is a method to replicate 2D or 3D of a pattern or shape, where a material is printed, pressed, or grown alongside the voids of a template. Usually, the template needs to be removed, parting the opposite of its pattern, which can be used as a template to achieve a replica of the original. Templating surface is the widely used method to prepare polymer surfaces because the method is quick, low cost, and efficient. Almost all things can be a template from natural bio surfaces to artificial structures. An oil-rebounding super-amphiphobic coating was made by using candle soot as a template, and the porous deposit of candle soot was coated with a 25 nm thick silica shell. The black coating became transparent after calcination at 600 °C. After salinization, the coating was super-amphiphobic with a water contact angle of 165°, sliding angle of 1° (Deng et al., 2012). The morphology of the porous structure and super-amphiphobic of the coating is presented in Figure 2.4.

Figure 2.4 Super-amphiphobicity of the surface. (A) a 2-ml water drop and (B) 5-ml hexadecane drop deposited on the surface possess a static contact angle of 165° T 1° and 156° T 1°, respectively; (C) cartoon of a liquid drop deposited on the fractal-like composite interface; (D) Time-resolved images of the bouncing of a 5-ml hexadecane drop on a super-amphiphobic surface (Deng et al., 2012).

Etching is the best way to construct rough surfaces, and the various methods include plasma etching, laser etching, chemical etching, and so on. The main feature of this method is that it is very fast, just needs several minutes to process. All the methods are significantly useful for the bio-mimic fabrication of the superhydrophobic surface. It can provide various surface functional groups and increase roughness to modify the wetting of a surface. Using the mixture of CHF₃ and
O2 gases after RF plasma etching, randomly distributed nano-craters were produced on a glass plate. Because of hydroxyl groups (-OH) on the surface, etched glass shows the hydrophilic property, and then hydrophobized by hepta-deca-fluoro-decyltri-chlorosilane (HFTS), which leads to superhydrophobicity with 92% transparency. The production of 100-200 nm in height and 80-400 nm in width nano-hair clusters on poly (methyl methacrylate) surfaces was fabricated using the mixture of pure oxygen and C4F8 gases and treated with a fluorocarbon to have the transparent and superhydrophobic property (Vourdas et al., 2007).

Another route is the combination of bottom-up with top-down approaches, including phase separation, electro-spinning, the casting of polymer solution, and so on. Phase separation is a good way to prepare a rough surface of multi-complex mixtures. Phase separation is not stable and can separate into two phases under effective cooling, one might be solid at any particular point in the process. Separation is induced by a dual-continuous structure with the formation of three-dimensional networks and their interpenetration is one of the possible ways. From the separation, the original structure is very fine but of reduced interfacial surface area; structures finally collapse for the two-layer formation and maybe more layers in presence of immiscible components. Environment factors, such as temperature, pressure, may result in remixing when the conditions revert. Casting a PLLA/dioxane solution on PLLA substrate, Song and coworkers induced phase separation of the polymer solution in a nonsolvent. Hierarchical microparticles were fabricated on the substrate and a contact angle is larger than 150° by increasing the surface roughness (Song et al., 2009).

Honeycomb-like microporous coatings of polymers with 500 nm to 50 um diameters have been fabricated with the casting of polymer solution under humid conditions. The coatings of honeycomb-patterned polymer produced by Yabu & Shimomura could be treated as a promising functional material including engineering and super-engineering plastics, biodegradable polymers, and titanium oxide (Yabu & Shimomura, 2005). Later on, they patented the honeycomb-patterned superhydrophobic films of fluorinated polymers with pore size greater than 1 um, but they were not transparent. Recently, a superhydrophobic SiO2/nylon 6, 6 nanocomposite coating was fabricated with a facile casting process. This coating showed a superhydrophobic property of pH ranging from 1 to 14, resulting in a water contact angle greater than 159°, but the sliding angles could be decreased to 1° with the content of SiO2 nanoparticles increasing (Y. Guo et al., 2011).
The method further is useful to other hydrophilic polymers for the preparation of superhydrophobic surfaces, and therefore, extends the use of such materials for super wetting applications. Superhydrophobic with transparent polymer functionalized CNT film was fabricated by one-step spray casting CNT-polystyrene suspensions. The film presented the water contact angle was 160° (as shown in Figure 2.5), and a slide angle was less than 3° (J. Yang et al., 2009).

![Figure 2.5 MWCNT-PS film; FESEM images (a) low magnification and (b) high magnification; (c) The rolling process of the water on the superhydrophobic MWCNT-PS film (J. Yang et al., 2009).](image)

2.2.3 Applications of Functionalizing Superhydrophobic Surfaces

Functionalized superhydrophobic coatings or membranes have been widely studied in recent years. PFDTs/CNT superhydrophobic membranes with controlled functionalization which could be used as an effective way to separate water and oil emulsion, and it has high separation efficiency under extreme conditions, which includes high and low temperature, strongly acidic or alkaline solutions (Gu et al., 2015). The coating of perfluoroalkyl silane was applied to change the surface properties of carbon nanotubes, which renders the films has superhydrophobic property and high mechanical strength (Georgakilas V, Bourlinos A B, Zboril R, et al. 2008). A novel superhydrophobic graphene aerogel with extremely low bulk density and high-water contact angle was produced with highly scalable, low-cost, and no requirement for supercritical drying (Y. Lin et al., 2011a). With the help of HFTMS, the graphene composite films with nano-scaled surface roughness showed superhydrophobic properties, and they could be used as biomaterials (Zhou et al., 2012). Because of the mechanical and thermal properties of graphene oxide, using graphene-based nanocomposites with top-down synthesis separate oil and water mixture (Smith et al., 2019).
Coating graphene oxide nanosheets with polydopamine (PDA) and subsequent reaction with 1\textit{H}, 1\textit{H}, 2\textit{H}, 2\textit{H}-perfluorodecanethiol, which leads functionalized sponge showed superhydrophobic property, high organic adsorption capacity, and oil/water separation under extremely conditions (Cao et al., 2019). The rGO-PDA-PFDT film showed superhydrophobic/superoleophilic properties, which could be worked as a membrane to separate oil and water mixture even under harsh environments such as acid and alkaline solvents, and the membrane could be reused for 10 repetitive cycles with high flux (Yuanyuan Cheng, Alexandre Barras 2019).

2.3 GRAPHENE

2.3.1 Introduction

Graphene, a single layer carbon atom of graphene bonded to each other with a sp² network and creates a two-dimensional honeycomb crystalline structure, has attracted considerable attention in both the scientific and industrial communities since the first isolation through mechanical exfoliation in 2004 (Novoselov, K. S., et al. 2004). The unique 2D honeycomb crystalline structure not only contributes to it being the thinnest and strongest material but also makes it has many excellent chemical and physical properties (Figure 2.6). These excellent properties of graphene include the Hall effect (Y. Zhang et al., 2005), bipolar electric field effect, relativistic Dirac fermions (Novoselov et al., 2005), high thermal conductivity (5000 W m⁻¹ K⁻¹) (Balandin et al., 2008), high transparency (97.7%) (Nair et al., 2008), superior carrier mobility at room temperature (200 000 cm²V⁻¹s⁻¹) (Bolotin et al., 2008), good electrical conductivity (2000 S m⁻¹) (Wu et al., 2009), extremely high theoretical specific surface area (2630 m² g⁻¹) (Stoller et al., 2008), excellent environmental compatibility, high mechanical strength with Young’s modulus of 1 TPa (C. Lee et al., 2008a), and high adsorption capacity for organic and inorganic molecules (Lazar et al., 2013). Also, graphene as a smart material, shows (S. Wan et al., 2013) tunable wettability characteristic (Rafiee et al., 2010).
Figure 2.6 The superior properties of pristine graphene (X. Li et al., 2016).

The remarkably high electrical properties of graphene make this material highly relevant for both high mobility and even ballistic transport applications as well as low-cost materials for transparent conductive materials such as liquid crystal cell electrodes. This specific aspect takes advantage of the electronic as well as optical properties of single-sheet graphene. The high mechanical strength makes these materials ideal candidates for mechanical reinforcement, and such a high sustainable tension in a single sheet, graphene has tremendous potential as the ultimately thin material for NEMS applications such as pressure sensors and resonators.

2.3.2 Applications of Graphene

Due to these above excellent properties, graphene has more promising applications in multi-fields, such as physical, biological, and engineering fields (Uddin et al., 2013). The pure graphene sheet has hydrophilic properties, and the edges of the two-dimension sheet are extremely reactive. It is easy to react with the hydroxyl groups under humidity, and then the edges obtain chemical stability after reaction (Lim et al., 2020). The wettability of graphene film can be switched from hydrophobic to hydrophilic due to different external stimuli (Lim et al., 2020). There are various methods to change the wettability of graphene, such as pH alteration (as shown in Figure 2.7), UV irradiation, thermal treatment, and so on (S. Wan et al., 2013). Changing graphene films from superhydrophobic to superhydrophilic was based on a certain concentration of acetone-water solutions (Rafiee et al., 2010). Because of its excellent physicochemical
properties, the wettability of graphene is switchable by functionalizing with modifying the surface energy (Dong et al., 2013). Graphene oxide film presented tunable wettability under photoinduced conditions, and graphene films obtained reversible wettability with light irradiation (X. Zhang et al., 2012). By combining with functional groups, such as hydroxyl, carboxyl, and carbonyl, graphene films showed hydrophilic property (Tong et al., 2018). But on the other hand, functionalizing graphene with hydrophobic functional groups, such as, methyl, fluorine, polymers, and inorganic particles, which indicates superhydrophobic property (Y. Lin et al., 2011b).

But all these advantages are due to the single-layer structure, so it is very important to produce single-layer graphene, there are advantages and disadvantages for the technique currently used to produce graphene, as shown in Table 2.1 (Caterina Soldano 2010.). The most effective way is the chemical oxidation-reduction of graphite because of its potential use for mass production and its ability to easily functionalize the surface of the graphene in various applications (Uddin et al., 2013). However, the stacking of graphene layers is the main problem for this method due to the van der Waals forces leading to the formation of a graphitic structure. In order to minimize the agglomeration of graphene sheets, it is essential to modify the surface of graphene oxide prior to reduction (Figure 2.8). Using some foreign stabilizer to functionalize graphene, such as small organic molecules and a low molecular weight polymer, can promote dispersibility in liquid solvents. The chemical moiety attached to the surface of graphene by non-covalent or covalent bonds increases the hydrophobic or hydrophilic property. Also, surface functionalizing graphene significantly improves the performance of electrochemical sensing and energy-related devices.
Table 2.1 Advantages and disadvantages for techniques currently used to produce graphene

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical exfoliation</td>
<td>Low-cost and easy, No special equipment needed, SiO₂ thickness is tuned for better contrast</td>
<td>Serendipitous, Uneven films, Labor intensive (not suitable for large-scale production)</td>
</tr>
<tr>
<td>Epitaxial growth</td>
<td>Most even films (of any method), Large scale area</td>
<td>Difficult control of morphology and adsorption energy, High-temperature process</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>Straightforward up-scaling, Versatile handling of the suspension, Rapid process</td>
<td>Fragile stability of the colloidal dispersion, Reduction to graphene is only partial</td>
</tr>
</tbody>
</table>

The roughness effect combined with the surface chemistry of the graphene sheets can be used to totally change the wettability of the substrate. By controlling the relative ratios of acetone and water in the solution, the water contact angle of the resulting graphene film can be switched in a wide range (from superhydrophobic to superhydrophilic). According to the high specific surface area of graphene, the functionalized superhydrophobic surface not only can be stretched up to 400% and withstand more than 1000 cycles of stretching-relaxation with superhydrophobic property, but also can be preserved during many kinds of damages, such as knife-scratch,
sandpaper abrasion, oil contamination, and thermal treatment (P. Wang et al., 2018). The superhydrophobic surface with electrochemically exfoliated graphene exhibits good mechanical stability even after water impact and sand impact tests (Wang, Peng, et al. 2017). The surfaces combined with polymer and inorganic nanoparticles show superhydrophobic properties, adding graphene endows high electrical conductivity and robust water adhesion capability (Z. Chen et al., 2013). Silicon wafers with microstructures, on which graphene nanosheets were grown and modified by a chemical method to form hydrophilic and hydrophobic structures, then the graphene surface could be switched from superhydrophilic and superhydrophobic (Dong et al., 2013).

2.4 GRAPHENE OXIDE (GO) AND REDUCED GRAPHENE OXIDE (rGO)

2.4.1 Introduction

Graphene oxide (GO) (Figure 2.9) was first synthesized by Brodie in 1859 (May & May, 1859). GO is a monolayer sheet, and the size of its sheet is polydisperse. The structure of graphene oxide is much more complicated than a graphene sheet, and the properties depend on its structure. GO is treated as a precursor for synthesizing graphene by either chemical or thermal reduction processes, and is the production of the chemical treatment of graphite through oxidation, and it can be produced with a high yield by modified Hummers’ method, which is cost-effective and cheap (Pei & Cheng, 2012). The main approaches for the synthesis of graphene oxide are shown in Table 2.2 (W. Yu et al., 2020a). It is different from graphene, there are various oxygen-containing functional groups presented in the GO, such as, hydroxyl, epoxy, carboxy, and carbonyl groups, which makes GO have highly hydrophilic properties. This attributes to GO has good dispersibility in many solvents, particularly in water. And the oxygenated groups in GO can strongly influence its electronic, mechanical, thermal, and electrochemical properties. In addition, graphene oxide has both aromatic (sp²) and aliphatic (sp³) domains, which leads to an increase in the type of interactions that can occur on the surface.
Figure 2. Preparation of graphene oxide (May & May, 1859).

Table 2. The main methods of synthesize graphene oxide (W. Yu et al., 2020a)

<table>
<thead>
<tr>
<th>Scientists</th>
<th>Reagent</th>
<th>Reaction time</th>
<th>Reaction temperature</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brodie</td>
<td>KClO₃, HNO₃</td>
<td>3-4 h</td>
<td>60°C</td>
<td>The first method</td>
</tr>
<tr>
<td>Staudenmaier</td>
<td>KClO₃, HNO₃, H₂SO₄</td>
<td>96 h</td>
<td>RT</td>
<td>N/A</td>
</tr>
<tr>
<td>Hummers</td>
<td>HNO₃</td>
<td>20 h</td>
<td>RT</td>
<td>Only using HNO₃</td>
</tr>
<tr>
<td>David</td>
<td>KMnO₄, NaNO₃, H₂SO₄</td>
<td>&lt; 2 h</td>
<td>35°C</td>
<td>Reaction time is short</td>
</tr>
<tr>
<td>Eigler</td>
<td>KMnO₄, NaNO₃, H₂SO₄</td>
<td>16 h</td>
<td>10°C</td>
<td>High quality rGO</td>
</tr>
<tr>
<td>Peng</td>
<td>K₂FeO₄, H₂SO₄</td>
<td>1 h</td>
<td>RT</td>
<td>No heavy metal manganese pollution</td>
</tr>
<tr>
<td>Marcano</td>
<td>H₂SO₄, H₃PO₄, KMnO₄</td>
<td>12 h</td>
<td>50°C</td>
<td>Low toxicity</td>
</tr>
<tr>
<td>Panwar</td>
<td>H₂SO₄, H₃PO₄, KMnO₄, HNO₃</td>
<td>3 h</td>
<td>50°C</td>
<td>High yield</td>
</tr>
<tr>
<td>Shen</td>
<td>Benzoyl peroxide</td>
<td>10 min</td>
<td>110°C</td>
<td>No liquid</td>
</tr>
</tbody>
</table>
Reduced graphene oxide (rGO) (Figure 2.10) is one form of GO that is processed by chemical, thermal, and other methods in order to reduce the oxygen content. There are many reduction methods, such as thermal, photocatalytic, and chemical reduction. In the past, researchers have created rGO from GO by:

- Treating GO with hydrazine hydrate and maintaining the solution at 100 for 24h.
- Exposing GO to a hydrogen plasma for a few seconds.
- Exposing GO to another form for strong pulse light, such as that produced by xenon flash tubes.
- Heating GO in distilled water at varying degrees for different lengths of time.
- Combining GO with an expansion-reduction agent such as urea and heating the solution to cause the urea to release reducing gases, followed by cooling.
- Directly heating GO to very high levels in a furnace.
- Linear sweep voltammetry.

Thermal reduction of GO includes the heating of GO at the temperature of more than 900 °C in an inert atmosphere for selective removal of hydroxyl groups (-OH), carboxyl groups (-COOH), and epoxy groups (=O) from GO (Saleem et al., 2018). But the heating process damages the structure of the graphene platelets as pressure builds and carbon dioxide is released, and also causes a substantial reduction in the mass of the GO, which creates imperfections and vacancies, and finally has an effect on the mechanical strength of the rGO produced. For photocatalytic reduction of GO, the light source such as sunlight (Mohandoss et al., 2017), UV light (Han et al., 2015), or xenon flash (Kang et al., 2018) is required with the intensity or affected region must be systematically controlled for an efficient reduction of GO. As for the chemical reduction of GO, the stirring or refluxing of the GO solution in the presence of a reducing agent at the specific reaction temperature is enough to promote the deoxygenation effect of GO, which shows the simple and method to prepare rGO (Kuang et al., 2018). However, the rGO produced by chemical reduction has often resulted in relatively poor yields in terms of surface area and electronic conductivity.
2.4.2 Applications of GO and rGO

During the process of production rGO, there are several ways to functionalize rGO for use in different applications. Treating rGO with other chemicals or by making new compounds by combining rGO with other 2D or 3D materials, can enhance the properties of the compound to suit more wide applications.

GO is a promising material for biological and electro-chemical applications due to its excellent aqueous processability, amphiphilicity, surface functionalizability, surface-enhanced Raman scattering property, and fluorescence quenching ability (Chung et al., 2013). One of the advantages of GO is its easy dispersibility in water and other organic solvents, as well as in different matrixes, according to the presence of oxygen functionalities, which is an important property when mixing the material with ceramic or polymer matrixes when trying to improve their...
electrical and mechanical properties. Due to the negative charge surface of GO and its large aspect ratio nanosheet structure, GO-based membranes can be used in gas barrier nanocomposites (Y. H. Yang et al., 2013). GO membranes are widely treated as an excellent material for wastewater treatment because of their high water permeability (Hu & Mi, 2013). It is an efficient material to be used in the photothermal conversion of light in nanocomposites (E. Wang et al., 2013). GO is a new material for gas sensing because of the functional groups on GO nanosheets, which can adsorb gas molecules, and the electric or optical properties of GO will change when exposed to certain gases (Toda et al., 2015). GO can be used in the biomedical field, especially in drug-delivery systems. GO is likely superior to many other anticancer drugs because it does not target healthy cells with low toxic, only tumors (X. Yang et al., 2011). GO combines with other polymers and forms nanocomposites, which enhance the properties of the original polymer, such as elastic modulus, tensile strength, and thermal stability. In the solid form, GO flakes attached to one another form thin and extremely stable paper-like structures, which can be folded, wrinkled, and stretched. These free-standing GO films can be used for hydrogen storage applications, ion conductors, and nanofiltration membranes.

rGO is the thinnest and the most lightweight 2D carbon material, which is a promising candidate for microwave absorbers (Lv et al., 2016). The structure of rGO is like graphene sheets and is an atomically thin sheet of carbon atoms, which usually bear transparent and wrinkled features under a microscope (Figure 2.11) (Bo et al., 2014). The property of rGO renders a thin film (less than 30 nm) of rGO semi-transparent to visible and thick films that are opaque. Therefore, rGO can be widely used for transparent conductor applications. Because rGO has minimized the number of oxygen groups, its properties are closer to those of pristine graphene (Pei & Cheng, 2012). rGO can be used as effective fillers in polymer nanocomposite materials due to its dispersibility in matrices and it also can improve the thermal conductivity of the resultant nanocomposites (Yoo et al., 2014). rGO presents excellent electrical conductivity when encapsulated in polymer matrices, which endows rGO/polymer nanocomposites with excellent electrical stimuli-responsive actuation (C. Yang et al., 2017). According to the superior electrical properties of rGO, it is also a promising material for many energy applications, such as in supercapacitors, stretchable electronics, and so on (D. Lin et al., 2016). The tight packing of sp² carbon atoms make it can be served as an excellent barrier to gas molecules (Tan & Thomas, 2016),
and also can be used in packaging materials, protection for sensitive electronic devices, or even corrosion-resistant materials (Ghauri et al., 2017).

Because of the extremely high surface area, GO and rGO can be used as electrode materials in batteries and double-layered capacitors, as well as fuel cells and solar cells (Y. Zhu et al., 2010). GO/rGO is a fluorescent material that could be used for biosensing applications, for early disease detection, and even for assisting in finding cures for cancer and detecting biologically relevant molecules. GO and rGO can be used as electronic devices, such as gas sensors (as shown in Figure 2.12), biosensors, and touch screen devices.

![Gas sensing with rGO sensor](image)

Figure 2.12 Schematic diagram of the rGO-based gas sensor device (Bo et al., 2014).

Adding graphene oxide nanosheet into polyhedral oligomeric silsesquioxane (POSS) shows superhydrophobic property, and also reveals excellent anti-corrosion performance, as well as the potential application for lubrication and settle the challenge of corrosion and wear (Ye et al., 2019). By reduction of the graphene oxide, the superhydrophobic surface with graphene obtained optical transparency of 72.7% and could be used as an electrode (J. S. Lee et al., 2013). Reduced graphene oxide coated melamine-formaldehyde (rGO @MF) based sponge was fabricated to separate oil and water mixture, and the sponge not only showed superhydrophobic property but also could be reused more than 10 cycles (Saha & Dashairya, 2018). A novel reduced graphene oxide (rGO)/Ni composite coating with pinecone-like micro/nanostructures was fabricated on stainless steel substrate, which showed superhydrophobic property, self-cleaning, anti-corrosive, and mechanically durable (Z. Bai & Zhang, 2020).
2.5 CARBON NANOTUBES (CNTs)

2.5.1 Introduction

Sumio Iijima accidentally discovered carbon nanotubes (CNTs) in 1991 when studying the surfaces of graphite electrodes (Iijima et al., 1991). These tiny carbon tubes are cylinder-shaped macromolecules with a radius as small as a few nanometers, which can be grown up to 20 cm in length (Balasubramanian & Burghard, 2005). CNTs generally have two types of nanotubes: multi-walled nanotubes (MWNTs) and single-wall nanotubes (SWNTs). An MWNT is combined with a concentric arrangement of many cylinders (Figure 2.13), and the diameter is 5 to 20 nm, and can even exceed 100 nm. The formation of an SWNT looks like rolling of a graphene sheet, and the diameter is 0.8 to 2 nm. According to the orientation of the tube axis with respect to the hexagonal lattice, the structure of a nanotube can be classified by its chiral vector (Figure 2.14), which is denoted by the chiral indices \((n, m)\). The classification of the nanotubes as armchair \((n=m)\) or zigzag \((m=0)\) has its origin from the geometric arrangement of the carbon atoms at the seam of the cylinders. While both these types of tubes possess mirror symmetry, nanotubes with \(m \neq n\) are chiral. The latter kind of tube exists as two enantiomers with right- and left-handed helicity. The nanotubes can be metallic or semiconducting based on their structural parameters. CNTs have high Young’s modulus and tensile strength, which makes them perfect composite materials with improved mechanical properties.
Figure 2. 13 Structure of a multi-walled carbon nanotube made up of three shells of differing chirality (Balasubramanian & Burghard, 2005).

Figure 2. 14 Roll-up of a graphene sheet leading to the three different types of CNTs (Balasubramanian & Burghard, 2005).
Nowadays, MWNTs and SWNTs are produced mainly by three techniques: arc-discharge, laser-ablation, and catalytic growth (Popov, 2004). For arc-discharge, an arc is generated in between two graphitic rods kept at a certain distance of a few mm (as shown in Figure 2.15), the carbon needles were grown on the negative end of the carbon electrode, and the needles range from 4 to 30 nm in diameter and up to 1 um in length. Transmission electron microscopy (TEM) indicated that each of the needles included coaxial tubes of graphitic sheets, ranging in number from 2 to about 50, later termed multi-walled carbon nanotubes (MWNTs).

In 1996, Smalley and co-workers produced high yields (> 70%) of SWNTs by laser ablation (vaporization) of graphite rods with small amounts of Ni and Co at 1200 °C (as shown in Figure 2.16). This method with a high-intensity laser beam is used for the sublimation of graphite and gives high-quality and high-purity nanotubes, but the disadvantages of the method are high-cost of synthesis, and it relies on very high temperature to evaporate.
Laser ablation scheme. Laser beam vaporizes the target of a mixture of graphite and metal catalyst (Co, Ni) in a horizontal tube in a flow of inert gas at controlled pressure and in a tube furnace at ~1200 °C. The nanotubes are deposited on a water-cooled collector outside the furnace (Popov, 2004).

Carbon filaments and fibers have been produced by chemical vapor decomposition (CVD) of hydrocarbons in the presence of a catalyst since the 1960s (Baker R T K.1989.). A similar method was used for the first time by Yacaman et al. in 1993 (José-Yacamán et al., 1993) and in 1994 Ivanov and co-workers to grow MWNTs (Ivanov V, Nagy J B, Lambin P, et al. 1994.). In recent years, the CVD technique has been gradually improved and optimized. In general, the CVD process contains catalyst-assisted decomposition of hydrocarbons, usually ethylene or acetylene, in a tube reactor at 550-750°C and growth of carbon nanotubes over the catalyst upon cooling the system (as shown in Figure 2.17). Best results are obtained with Fe, Ni, or Co nanoparticles as catalysts.

One exceptional property of CNTs is chemical stability, which allows for the selective and controlled covalent functionalization of the nanotubes. There are two main methods considered for the surface modification of CNTs (Figure 2.18). One is the noncovalent attachment of molecules; the second is the covalent attachment of functional groups to the walls of CNTs. The
noncovalent attachment is mainly bonded by van der Waals forces and must be with thermodynamic criteria. The advantage of noncovalent attachment is that the structure of CNTs is not changed, so their mechanical properties should be the same. But the forces between the wrapping molecule and CNTs might be weak, and the efficiency of the load transfer must be low. The covalent attachment of CNTs can improve the efficiency of load transfer. However, the functional groups may lead to defects on the walls of the perfect structure of the nanotubes, which will decrease the strength of the reinforcing component (Eitan et al., 2003).

Figure 2. Possible sites for functionalization and functionalization processes for CNTs: (a) covalent sidewall functionalization, (b) functionalization at defective sites, (c) noncovalent functionalization by surfactants adsorption, (d) wrapping of polymer chains, and (e) encapsulation of region materials (Hirsch, 2002).
2.5.2 Applications of CNTs

Nanotubes are useful as electron field emitters due to their nano size, structural perfection, high electrical conductivity, and chemical stability with an application in flat panel displays (Tomanek et al., 1995). CNTs have large surface area, unique high mechanical, electrical, and thermal properties, which makes them attractive for applications in scientific and technological fields (as shown in Figure 2.19). The use of CNTs as fillers in different materials to fabricate nanocomposites is one of the most developed fields in nanotechnology. The main idea for incorporating CNTs into different polymeric and other materials is to improve the properties of these materials. The high Young’s modulus and tensile strength of CNTs attribute to their potential use in composite materials with improved mechanical properties (Overney et al., 1993). Due to high electrical conductivity, and chemical stability, CNTs are suitable as electron field emitters. This can be done when a potential is applied between the CNTs surface and the anode. Electrons are easily emitted from their tips because of the curvature present in the CNTs in the form of pentagons or due to the presence of oxidized tips. MWNTs can be used to electro-catalyze an oxygen reduction reaction, which is vital for fuel cells (Tomanek et al., 1995). SWNTs have large irreversible capacities and voltage hysteresis, which makes them can be used as battery electrodes (Che et al., 1998). They indicated that by damaging the surface of the SWNTs chemically or mechanically, one can increase the electrochemical storage of these batteries. According to their hollow cylindrical nature, CNTs can be treated as efficient gas and metal containers, resulting in the high and reversible hydrogen adsorption of SWNTs, they can be used as high-capacity hydrogen storage media (Klangt et al., 1997). Single-walled CNTs network films can be used to separate emulsified oil and water mixtures with a high flux (S. J. Gao et al., 2014). The electronic properties of SWNTs showed that SWNTs could be either metallic or semiconducting materials (Mintmire et al., 1992).
The superhydrophobic property will disappear when exposed to hot water (e.g., > 55°C), or hot water superhydrophobicity will be maintained when the superhydrophobic surface temperature is higher than that of the water droplet. However, adding CNTs develops the superhydrophobic surface coating that repels hot water without any limitation to the surface temperature. SEM indicated that nanostructures formed by CNTs, contributing both a high porosity and a small water droplet contact area, will maintain superhydrophobic property even for hot water (F. Wan et al., 2015). Superhydrophobic polyvinylidene fluoride-co-hexafluoropropylene (PcH) nanofibers membranes were produced by combing with a certain concentration of CNTs, which contributes to the membranes with high porosity, adequate pore sizes and narrow pore size distribution, and thin thickness. And the membranes could be used for direct contact membrane desalination application (Tijing et al., 2016). Conductive superhydrophobic cotton fabric was produced through assembling carboxylated and aminated MWNTs and modifying them with polydimethylsiloxane. This material can be used in oil-water separation with high efficiency and great reusability. Moreover, the conductive fabric-based pressure sensor presented stable and regular responses in human motion detection containing finger bending, wrist movement, walking, and running, and the pressure sensor could work even under wet and humid conditions (L. Zheng et al., 2019).
3. CARBON-BASED REINFORCEMENTS OF SUPERHYDROPHOBIC POLYMERS

Traditional bulk superhydrophobic materials are fragile and easy to break, and the strength decreases with the decrease of surface energy, so it is very challenging to achieve a bulk superhydrophobic material with high strength and mechanical durability. Carbon-based nanomaterials are ideal materials to reinforce the pure bulk superhydrophobic materials. The water contact angles of all new synthesized carbon-based reinforcements of superhydrophobic polymers are greater than 150°, and the surface energies are less than 1 mJ/m². The mechanical durability can be indicated by the nanoindentation technique and wear testing. Young’s modulus and hardness are greatly increased at micro-scale, which can be confirmed by nanoindentation technique, and Young’s moduli and hardness of new materials at 0.3 wt.ppt can achieve up to 7 GPa and 0.15 GPa at depth of 15 μm, respectively. The mechanisms of reinforcements are physically tangled with each other because of ultrasonic waves and chemically bonded due to the functional groups on the edge of carbon-nanomaterials, which could be indicated via scanning electron microscopy with energy dispersive spectroscopy. The fibers at micro/nanoscales improve the strength of superhydrophobic materials without changing the surface energy.
3.1 INTRODUCTION

Superhydrophobicity is found in nature, like lotus leaves, red rose petals, desert beetle, fish scales, etc. (Parvate et al., 2020) (Celia et al., 2013) Due to these natural structures, more and more artificial superhydrophobic structures are designed and created by mimicking the natural water-repellent surfaces. A superhydrophobic surface means the water contact angle is greater than 150° and the contact angle hysteresis is very low (less than 10°), which makes a water droplet bounce off the surface when there is a very slight tilting and contributes to superhydrophobic surfaces being widely used in industrial and biological fields (Webb et al., 2014a) (Y. Bai et al., 2021). Superhydrophobic materials have potential applications in anti-icing, self-cleaning, water-oil separation, etc. (Simpson et al., 2015a) (Manoharan & Bhattacharya, 2019) Superhydrophobic coatings and membranes are widely used in the practical field (Banerjee et al., 2015). However, mechanical durability is a big challenge for coatings and membranes to be daily used.

Researchers have tried different ways to improve the mechanical stability of superhydrophobic coatings. There are two main strategies to deal with the problem. The one is the self-healing method, which means superhydrophobicity could be recovered after being lost. Esteves et al. (Esteves et al., 2014) has reported a robust superhydrophobic coating with an all-in-one dispersion by a simple drop-cast method, which can recover the surface chemical composition spontaneously to re-achieve superhydrophobicity after being damaged. Tian et al. (Tian et al., 2016) has put forward a healable superhydrophobic coating exploiting the thermal degradation of silicones. The other strategy is increasing adhesive between coatings and substrates. Si et al. (Si et al., 2017) has designed a coating by increasing the adhesion strength between micro-nanoscale particles and their substrate with adhesives, but superhydrophobicity is lost when the adhesion strength is lower than the mechanical abrasion. Lu et al. (Y. Lu et al., 2015) has created a superhydrophobic coating by forming a paint and increasing adhesives to bond the paint.

However, the top superhydrophobic coatings and membranes are easy to wear off even they have lots of advantages. Recently, some scholars have developed bulk superhydrophobic materials. Bulk superhydrophobic materials could maintain superhydrophobicity because the surface is still superhydrophobic even if the top surface is worn off. Zhu et al. (X. Zhu et al., 2012) has fabricated superhydrophobic CNTs-PTFE bulk materials, which possess low-surface-energy microstructures extending throughout their whole volume. The superhydrophobic property of the
buck material was maintained after 20 abrasion cycles and even after cutting deep into it. A damage-tolerant superhydrophobic bulk material has been designed by Zhang et al. (X. Zhang et al., 2014), and the bulk materials retain the durable superhydrophobic property upon wear damage until they are worn out. However, the strategies to obtain durable superhydrophobic bulk materials are very expensive and complicated, and most of them are not friendly to the environment.

The mechanical durability of superhydrophobic bulk material is related to the surface topology and the surface chemistry (Ma & Hill, 2006). Generally, superhydrophobic bulk materials have very low surface energy throughout their entire volume. When these bulk materials are fabricated, the stronger bonds lead to an increase in surface energy which may cause much larger increases in fracture energy. This is due to an increase in bulk energy dissipation during fractures (Packman, 2003), and the weak cohesive forces make the bulk superhydrophobic materials very fragile. Roughing the surface is the other way to improve the superhydrophobic property, but also means just a very small portion of the overall area is in contact with the liquid. This can make the surface fragile and highly susceptible to abrasion (D. Wang et al., 2020a). Both of the above-stated factors lead to superhydrophobic bulk materials being fragile and poorly resistant to wear. In order to deal with the problem, various approaches have been explored, but most methods modestly improved the robustness. As an alternative method, this paper introduces nanomaterials to address the problem.

Adding nano-scale carbon-based materials into pure superhydrophobic hybrid organic-inorganic polymer (SHOIP) not only helps to tune the surface energy and control texture (Peng et al., 2018), but also offers them novel and special properties. In this paper, carbon-based nanomaterials include graphene (GP), graphene oxide (GO), reduced graphene oxide (rGO), and multi-walled carbon nanotubes (MWCNTs). Carbon-based nanomaterials have a high surface-to-volume ratio and possess exceptional electronic, thermal, and mechanical properties (Yoo et al., 2014) (W. Yu et al., 2020b). Carbon-based nanomaterials have been widely used as reinforcing fillers to enhance the physical and mechanical properties of polymers (Charoenchai et al., 2020) (D. Chen et al., 2012). The hypotheses are that carbon-based nanomaterials not only fill micropores but also can work as bridges between narrow cracks (J. Chen & Akono, 2020) (Y. Lin et al., 2011b).

Graphene is a two-dimensional honeycomb crystalline structure that is bonded to each other with a sp² (aromatic) network (Bellunato et al., 2016). The unique 2D structure not only
makes it the thinnest and strongest material but also has many excellent chemical and physical properties (Novoselov et al., 2005). GO and rGO are also 2D materials with a sp² network but GO has different properties. The structure of GO is much more complicated than a graphene sheet and the properties are related to its structure (Pei & Cheng, 2012). In addition, GO has aliphatic (sp³) domains which will contribute to an increase in interactions that occurred on the surface (W. Yu et al., 2020a). Because different kinds of oxygen-containing functional groups are presented in the GO, such as hydroxyl, carboxy, epoxy, and carbonyl groups, GO has highly hydrophilic properties, which makes it can be well dispersed in many solvents, especially in water. rGO can be processed by chemical, thermal, and other methods to reduce the oxygen content, therefore, its properties are closer to those of pristine graphene, but it is still one form of GO (Ghauri et al., 2017). Because of the unique structure of rGO, it becomes the thinnest and the most lightweight 2D carbon material. (Carbon nanotubes) CNTs are one-dimensional (1D) and cylindrical graphene layers of sp²-bonded carbon atoms, which contributes to the exceptional mechanical and electronic properties of carbon nanotubes (Q. Wang & Liew, 2009). The hollow tubes with unsealed ends possess a large amount of hydroxyl and carboxyl groups, which leads to high reaction activities. The nanotubes can be used for composite materials to improve mechanical properties with high young’s modulus and tensile strength (Vaisman et al., 2006).

Wang et al. (P. Wang et al., 2018) has put forward a stretchable and super-robust graphene superhydrophobic composite, and the graphene composite could withstand the abrasion by sandpaper for 20 m with maintaining the superhydrophobic property. Superhydrophobic polyhedral oligomeric silsesquioxane functionalized graphene oxide was synthesized by Ye et al. (Ye et al., 2019), and the material not only has high mechanical property but also possess outstanding anti-corrosion and wear-resistant abilities. Zhu et al. (X. Zhu et al., 2012) has fabricated novel superhydrophobic bulk materials by adding carbon-nanotubes to solve the mechanical damage and oil fouling problems, but this method needs high pressure and temperature. According to the above literature, carbon-based nanomaterials are promising materials to maintain the superhydrophobic property. In this paper, the bulk superhydrophobic materials are synthesized with carbon-based nanomaterials via a facile, and green method.
3.2. MATERIALS AND METHODS

3.2.1. Materials

The as-received dry powder of PowerPozz™ metakaolin (MK, Al₂O₃·2SiO₂, Advanced Cement Technologies, LLC., WA, USA) was used as the raw material for alkali activation, and its particle size distribution measured by the relevant ASTM standard method and chemical composition are shown in Table 3.1. The alkaline activator consisted of a mixture of sodium silicate solution (Na₂O·SiO₂·5H₂O, Ricca Chemical Co., TX, USA) and sodium hydroxide (NaOH, Fisher Scientific, Inc., USA). The former was a technical-grade solution with a 40º -42º Baumé (i.e., an average density of 1.4 g/cm³ or specific gravity of 1.38 to 1.42 at 25°C) and pH 11.2, and consisted of 9.1, 29.2, and 61.7 wt.% Na₂O, SiO₂, and H₂O, respectively (Table1), while the latter was white solid pellets with a ≥98% purity quotient. A trifunctional alkoxysilane (i.e., T silane), nitrogen-flushed methyltrimethoxysilane (MTMS, CH₃Si(OCH₃)₃, 97%, Acros Organics, Inc., NJ, USA), was selected as the hydrolysable agent to lower the surface energy via introducing the -SiCH₃ moieties to the siloxane. Carbon-based nanomaterials include graphene nanoplatelets (Strem Chemicals, Inc., MA, USA) with a nominal thickness and length of 6-8 nm and ~25 µm respectively, graphene oxide (GO, Tokyo Chemical Industry CO., LID) with the thickness and the width of 6-14 nm, ~20 µm respectively, reduced graphene oxide (rGO, MSE Supplies LLC., WA, USA) with the thickness and the width of 6-14 nm and ~20 µm respectively, and multi-walled carbon nanotubes (MWCNTs, Fisher Scientific, Inc., USA) with the diameter and length of 60-100 nm and ≥ 5 µm respectively.
Table 3. Chemical compositions of the metakaolin, sodium silicate solution, and methyltrimethoxysilane (MTMS) used for the synthesis of the siloxane (unit: wt.%).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Metakaolin</th>
<th>Na-silicate solution</th>
<th>MTMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay-sized fraction (≤ 2 um)</td>
<td>38.30</td>
<td>29.2</td>
<td>42.8</td>
</tr>
<tr>
<td>Silt-sized fraction (2-75 um)</td>
<td>58.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand-sized fraction (≥ 75 um)</td>
<td>2.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.61</td>
<td>29.2</td>
<td>42.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>39.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.13</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td>LOI*</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>98.46</td>
<td>100.0</td>
<td>42.8</td>
</tr>
</tbody>
</table>

*LOI = loss on ignition

3.2.2. Synthesis of Carbon-based Nanomaterials Reinforced T/Q Siloxanes

The general process for the synthesis of the T/Q siloxane consisted of alkali activation of the amorphous aluminosilicate (i.e., MK), hydrolysis of the T-silane MTMS, and co-condensation of alkali-activated silanols and Na-aluminols as well as hydrolysis-generated silanols. The T/Q siloxane was pre-designed to have a fixed nominal Si/Al, Na/Al, and T/Q molar ratio of 1.7, 1.0, and 0.0625, respectively. The silicon in the Si/Al ratio included the Si from both the trifunctional (T, RSiO₃/2, where R is an organic radical) and tetrafunctional (Q, SiO₄/2) structural units. As discussed later, such a T/Q siloxane was superhydrophobic due to the grafting of methy (i.e., -CH₃) groups into the Al-siloxanes and hence had little strength or fracture resistance, as indicated by the fact that the completely cured sample could be crushed with finger pressure of self-crack naturally during curing and drying. Therefore, to improve their mechanical properties, carbon-based nanomaterials were used as the reinforcing additives, which were added after alkali activation and hydrolysis, but prior to condensation or complete hardening of the precursor slurry.

The synthesis procedure started with preparing the alkaline activator solution (Figure 3.1) by dissolving NaOH pellets in deionized water, followed by adding the desired amount of sodium
silicate solution. Upon complete cooling of the mixture to the room temperature, MK powder was added to the activator solution, followed by continuous mixing for 25-30 min to achieve complete MK dissolution (i.e., alkali activation reaction), resulting in a homogenized viscous slurry containing activated silanos (Si(OH)$_4$) and Na-aluminols (NaAl(OH)$_4$). Then the desired amount (i.e., a pre-designed T/Q ratio of 0.0624 or 1/16) of MTMS was added dropwise via a pipet to the slurry while it was being continuously stirred to facilitate the uniform distribution of the MTMS. This step usually took 20-30 min to complete and was followed by at least 15 min continuous stirring to promote the breakdown and hydrolysis of the initially immiscible MTMS droplets. Finally, carbon-based nano particles were added to the above slurry at reinforcement levels of 0.3 wt.ppt (parts per thousand in weight), 3 wt.ppt, and 9 wt.ppt. Then followed by 25 min ultrasonication for better dispersion using an FS60 bath-type ultrasonic cleaner (Fisher Scientific, Inc., USA) that generated 100 W 42 kHz ultrasound waves. As carbon-based powders have a black color, the final composite precursor was a black homogenous slurry. Since the synthesis of the T/Q siloxane involved adding water and liquid T silane as well as generating highly volatile methanol and curing and drying led to the loss of water and methanol, it made little sense to use the total mass of all raw source materials (i.e., including water) used in the synthesis as the basis to calculate the content of carbon-based nanomaterials. Instead, the content of carbon-based nanomaterials was determined as the mass ratio (e.g., expressed as a percentage) of the mass of pure carbon-based nanomaterials to that of the completely cured and dried T/Q siloxane.
MK: metakaolin
MTMS: methyltrimethoxysilane

Figure 3.1 Synthesize procedures of MMG, MMGO, MMrGO, and MMWCNTs.

The final homogenized slurry was then cast into half-split cylindrical high-density polyethylene molds with an inner diameter and height of 25.4 and 63.5 mm respectively, which were coated with a thin layer of vacuum grease on the inner surface to facilitate subsequent demolding (Figure 3.2). The slurry samples in the molds were initially cured in an oven at 75°C for 7 days or until they became stiff enough for handling, followed by demolding and further curing in open atmosphere for at least additional 7 days or until they were dried completely, as verified by no further change in their mass. Table 3.2 summarizes all different contents of carbon-based materials used in this study, each with its specific designation (i.e., sample ID as shown in Table 3.4). For example, a pure siloxane with multi-walled carbon nanotubes was named MMWCNTs,
the first “M” means MK, the second “M” means MTMS, and WCNTs means multi-walled carbon nanotubes.

Figure 3. 2 Molds for curing samples: (a) a completely disassembled mold showing the two split half cylinders and two end caps; (b) a fully assembled mold with a cured sample.

Table 3. 2 Carbon-based nanomaterials at reinforcement levels

<table>
<thead>
<tr>
<th>Carbon-based nanomaterials</th>
<th>0.3 wt.ppt</th>
<th>3 wt.ppt</th>
<th>9 wt.ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene, g</td>
<td>0.036</td>
<td>0.36</td>
<td>1.08</td>
</tr>
<tr>
<td>MWCNTs, g</td>
<td>0.036</td>
<td>0.36</td>
<td>N/A</td>
</tr>
<tr>
<td>Graphene oxide, g</td>
<td>0.036</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Reduced Graphene Oxide, g</td>
<td>0.036</td>
<td>0.36</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3. 3 Polar and dispersive surface energy components of the test liquids

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_\ell$ (mJ/m$^2$)</th>
<th>$\gamma_{\ell}^P$ (mJ/m$^2$)</th>
<th>$\gamma_{\ell}^D$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>72.8</td>
<td>51.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Diiodomethane (DIM)</td>
<td>50.8</td>
<td>0.0</td>
<td>50.8</td>
</tr>
</tbody>
</table>
3.2.3. Sample Preparation

To avoid the errors which were led by the experiments, the above completely cured and dried cylindrical samples were divided by a carbide blade saw into three horizontally equal sections, namely Top, Middle, and Bottom (Figure 3.3a). For each of the three sections, a thin disk of ~5 and 25.4 mm in thickness and diameter respectively was trimmed for subsequent nanoindentation testing (Figure 3.3b). For nanoindentation test in this paper, each sample was chosen from Middle part.

Figure 3.3 The samples for tests: (a) the schematic of MMG at three different layers; (b) the polished thin disk for the nanoindentation testing obtained from each layer.

The thin disks used for nanoindentation testing required fine polishing. After preliminary manual polishing, each disk was first mounted onto a cylindrical aluminum puck of 25.4 mm in diameter (i.e., a standard sample stage for the G200 nanoindenter used in this study) with the Crystalbond 509 amber resin (Aremco Products, Inc., NY, USA) as the mounting adhesive that melts at 130°C and hardens upon cooling. Then such mounted disk specimen was successively polished in a MetaServ 250 polisher (Buehler Inc., Lake Bluff, IL, USA) by firstly abrasive Buehler’s CarbiMet and MicroCut silicon carbide grinding papers with grit sizes decreasing
successively from P180 to P4000 (i.e., P180, P280, P400, P800, P1000, P1200, P1500, P2500, and P4000 with the equivalent grit sizes of 78, 52, 35, 22, 18, 15, 13, 8, and 5 µm, respectively) and secondly alumina lapping films with grit sizes decreasing from 3.0, 1.0, to 0.3 µm to acquire a smooth and flat surface. Based on prior experience, the root-mean-square roughness \( R_{\text{rms}} \) of such polished rock specimens measured by atomic force microscopy is < 150 nm. Also, each time when changing the abrasive paper, filtered pressurized air was used to remove the polishing debris and dust from the polished surface. All polishing used no water or oil, and the slowest rotation speed and frequent pause to avoid generating excessive heat that might damage the samples.

3.2.4. Water Contact Angle Measurements

To examine the hydrophobicity, static water contact angles (WCA) were measured in a Dataphysics OCA 15 EC contact angle measurement system. A 10 µL water drop was dispensed by a syringe needle and static images immediately captured and then analyzed. Five different areas of the sample surface were measured with the sessile drop method and then calculated the averages of the WCA (shown in Table 3.4 and Figure 3.4). All measurements were performed at room temperature and atmospheric pressure.

The surface energy (\( \gamma \)) of our samples can be calculated with Fowkes Model. Fowkes’ surface energy theory was combined with the Young and Young-Dupree equations (Informática & Gittleman, 2014). This theory treats liquid and solid surface energy as polar and dispersive (nonpolar) components, and in this paper, water and diiodomethane were chosen as the test liquids (shown in Table 3.3).

\[
\frac{\gamma_l (\cos \theta + 1)}{2} = \sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}
\]  
\(3.1\)

where \( \gamma_l^d \) and \( \gamma_l^p \) are the liquid dispersive and polar components, respectively, and \( \gamma_s^d \) and \( \gamma_s^p \) are the solid dispersive and polar components, respectively.

The assumption is that the total surface energy is the sum of the dispersive and polar components as shown in Equation (3.2).

\[
\gamma_s = \gamma_s^d + \gamma_s^p
\]  
\(3.2\)
The calculated surface energies of carbon-based reinforcements of superhydrophobic polymers are presented in Table 3.4.

Figure 3.4 Water contact angles: (a) water contact angle for the smooth surface of powder SHOIP; (b) water contact angle for the smooth surface of solid SHOIP; (c) water contact angle for the smooth surface of solid MMG at 0.3 wt. ppt; (d) water contact angle for the natural surface of powder SHOIP; (e) water contact angle for the natural surface of solid SHOIP; (f) water contact angle for the natural surface of solid MMG at 0.3 wt. ppt; (g) water contact angle for the smooth surface of solid MMWCNTs at 0.3 wt. ppt; (h) water contact angle for the smooth surface of solid MMrGO at 0.3 wt. ppt; (i) water contact angle for the smooth surface of solid MMGO at 0.3 wt. ppt; (j) water contact angle for the natural surface of solid MMWCNTs at 0.3 wt. ppt; (k) water contact angle for the natural surface of solid MMrGO at 0.3 wt. ppt; (l) water contact angle for the natural surface of solid MMGO at 0.3 wt. ppt.
Table 3. 4 Water contact angle and surface energy

<table>
<thead>
<tr>
<th>Samples</th>
<th>Water Contact Angle (°)</th>
<th>Diiodomethane Contact Angle (°)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHOIP</td>
<td>162.6 ± 0.5</td>
<td>156.4 ± 0.4</td>
<td>0.091</td>
</tr>
<tr>
<td>MMWCNTs (0.3 wt.ppt)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>157.2 ± 0.3</td>
<td>146.5 ± 0.5</td>
<td>0.351</td>
</tr>
<tr>
<td>MMG (0.3 wt.ppt)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>156.3 ± 0.4</td>
<td>145.6 ± 0.3</td>
<td>0.368</td>
</tr>
<tr>
<td>MMrGO (0.3 wt.ppt)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>153.7 ± 0.2</td>
<td>141.2 ± 0.4</td>
<td>0.619</td>
</tr>
<tr>
<td>MMGO (0.3 wt.ppt)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>151.5 ± 0.2</td>
<td>138.3 ± 0.3</td>
<td>0.816</td>
</tr>
</tbody>
</table>

<sup>a</sup> First M means MK, the second M means MTMS, and WCNTs mean multi-walled CNTs

<sup>b</sup> MK, MTMS, and GP

<sup>c</sup> MK, MTMS, and rGO

<sup>d</sup> MK, MTMS, and GO

3.2.5. Fourier Transform Infrared Spectroscopy (FTIR)

To achieve the infrared spectrums of powder samples, Fourier transform infrared spectroscopy (FTIR, IR Tracer-100 FT-IT spectrometer, Shimadzu Corp., Kyoto, Japan) was used to analysis the samples. The system has very high excellent sensitivity with an SN ratio of 60,000:1, a high resolution is at 0.25 cm<sup>-1</sup>, and the high speed scanning capability is 20 spectra/second. In this paper, the IR spectra in the range of 4000-600 cm<sup>-1</sup>.

3.2.6. Ultra-Small-Angle X-ray Scattering (USAXS)

USAXS is a nondestructive measurement test in which the elastic scattering of X-rays from heterogeneous within a sample is recorded at low scattering angles. USAXS data include information about parameters, like the size, shape, volume, and total surface area of the scatters, as well as the characteristic distances between those scatters that are ordered or partially ordered. All data in this paper were achieved from the USAXS instrument at the Advanced Photo Source (APS) at Argonne National Laboratory (Lemont, IL, USA). The instrument has angular and energy resolutions of the order of 10<sup>-4</sup>, accurate and repeatable X-ray energy tunability over its operational
energy range from 8 to 18 keV, and a dynamic intensity range of $10^8$ to $10^9$, according to the configuration. The scattering vector range is between 0.0001 to 1 Å$^{-1}$.

USAXS is an excellent tool to quantitatively characterize the morphology of materials on length scales from 0.1 to 50 µm. Some previously undetected morphological features can be revealed with this technique. In this paper, the finely-ground powder was prepared by hand-grinding a piece of sample in a mortar and pestle to pass all material through a #625 mesh (i.e., an opening size of 20 µm), followed by putting samples in washers to test.

3.2.7. Nanoindentation Technique

All nanoindentation tests in this paper were conducted in a Keysight G200 nanoindenter (Keysight Technologies, Inc., Santa Rosa, CA, USA) equipped with a pre-calibrated Berkovich diamond tip of < 20 nm in tip radius and of ~25 µm in effective depth and an electromagnetic load sensor of 625 mN in capacity. The load was applied at a constant indentation strain rate $\dot{h}/h$ (where $h$ is the indentation depth) of 0.05 s$^{-1}$ under the continuous stiffness measurement (CSM) mode with an acceptable thermal drift rate of < 0.05 nm/s. The premium targeted maximum depth set for all measurements is 15 µm. However, depending on the tested material’s properties, certain indent measurements might stop prior to reaching the $h_{\text{max}}$ of 15 µm if the applied load exceeded the load sensor’s capacity (i.e., 625 mN). The reason for selecting such a large maximum indentation depth was four-fold: (1) to eliminate the potential negative interference of surface roughness as well as micropores of the samples with the measurement; (2) to characterize the depth-dependent variability of the tested samples; (3) to account for the possible localized effects of the carbon-based nanomaterials in nominal length; and (4) to enable the extraction of the mesoscale or macroscale properties of the samples, at least for the elasticity, since the elastically deformed zone beneath the indenter tip is roughly ~10 $h_{\text{max}}$ (i.e., a zone with a diameter of ~150 µm should encompass enough carbon-based nanomaterials as well as some microstructure features such as micropores of the tested samples). The CSM loading mode involved the superposition of a harmonic oscillation of 2 nm and 45 Hz in amplitude and frequency respectively over the monotonic, constant indentation strain rate loading process. Upon reaching the maximum depth, the load was held constant for 60 s, followed by monotonic unloading at a constant loading rate that was the same as the one at the maximum load $F_{\text{max}}$. When the load decreased to 10% of $F_{\text{max}},$
unloading was stopped and the load was held constant for 10 s to record the thermal drift, followed by complete unloading.

For each sample, to get more converge and accurate data to analyze, the number of indents needs to be 100. Therefore, each sample was arranged in a $10 \times 10$ grid nano-indentation with a spacing of 300 $\mu m$ between two adjacent indents to prevent negative interference from each other (Sudharshan Phani & Oliver, 2019), such a grid covered an area of more than $2700 \mu m \times 2700 \mu m$. In general, the indentation load and depth were recorded with time, and the data analyzed by the widely accepted Oliver and Pharr method (Oliver & Pharr, 1992) to derive the samples’ hardness $H$ and Young’s modulus $E$. A constant Poisson’s ratio of 0.3 was assumed for all tested samples, since the error of this parameter usually results in a very small or negligible variation in the sample’s Young’s modulus. Furthermore, the successful, valid measurements out of the 100 indents were averaged to obtain the mean and the standard deviation of each sample.

### 3.2.8. Wear Testing

Figure 3.11. (a) presents the set-up of the abrasion test. The sample was pressed onto a piece of silicon carbide sandpaper (Grit No. 220) under a pressure of 21.2 kPa. The sandpaper moved back and forth over the same line of contact with the assistance of the spring set and then abraded for a roundtrip of 50 mm as one cycle. The pressure applied on the surface can be adjusted by changing the pressure gauge, and the number of cycles can be recorded with a computer. In this paper, the wear effects mainly focus on the mechanical durability of the new materials. That means the difference in thickness changes with cycles under the wearing conditions.
3.2.9. Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)

The surfaces of the materials were observed by field emission scanning electron microscopy (SEM) in an FEI Magellan 400 XHR-SEM (Thermo Fisher Scientific, Inc. Hillsboro, OR, USA) at a low voltage of 5 keV beam voltage and appropriate beam current. The working distance is 4 mm. For the examined samples, it was not necessary to apply the conductive coating on the sample surface because the electron beam was generated at a low voltage and small current. The elemental composition of the samples can be performed by energy dispersive spectroscopy (EDS) in an FEI Magellan 400 XHR-SEM.

Figure 3.5 Idealized structures of graphene oxide and reduced graphene oxide.

3.3. ANALYSES OF RESULTS

3.3.1. Superhydrophobocity

Figure 3.4 presents the superhydrophobic nature (i.e., characterized by a WCA of > 150º) of both pure and carbon-based nanomaterials reinforced T/Q siloxanes. The former has a WCA of ~162.6º (Figures 3.4a and 4d) and 165.4º (Figures 3.4b and 4e) for the dry powder and solid block of SHOIP respectively, indicating that the pure T/Q siloxane is superhydrophobic. As shown in Figures 3.4c, 4f, and 4g-4l, adding 0.3 wt.% carbon-based nanomaterials into the T/Q siloxane slightly decrease the WCA, and the lowest WCA is 151.5º, confirming that the composites are still superhydrophobic. Moreover, simple visual examinations found that nearly spherical water droplets form on any fractured surfaces and on the ground dry powder (Figures 3.4d-4f and 4j-4l),
further suggesting that the synthesized siloxanes have three-dimensional (3D) voluminous superhydrophobicity.

In general, a superhydrophobic surface with a WCA of > 150º results from two important features: (1) the surface material or layer must possess low surface energy, usually due to the presence of non-polar moieties (e.g., nonpolar functional groups such as -CH₃, -CF₃, -SiO₄); (2) the surface has hierarchical roughness, usually at multiple scales (Michael & Bhushan, 2007). In fact, currently achievable maximum WCA of a smooth surface is ~119 to 120º, from a manufactured material with its surface covered by fluorocarbons (i.e., -CF₃). The obtained WCA data confirm that the siloxane’s interior surface is full of -SiCH₃ groups that decrease the chemical energy and obvious hierarchical roughness that further enhances the hydrophobicity.
According to Figure 3.6, the characteristic peaks for all materials were observed at almost 1450 cm\(^{-1}\) owing to C-H stretching, which means the surfaces of all materials are covered with -CH\(_3\) groups leading to superhydrophobic property.

Figure 3. 6 FTIR spectra for all reinforcement materials at 0.3 wt.ppt and SHOIP.
3.3.2. Results from Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.6 presents the FTIR spectrums for all materials. The characteristic peaks for SHOIP were observed at 870 and 1010 cm\(^{-1}\) owing to Si-O-Al stretching, Si-O-Si symmetric stretching, respectively, which resulted from the aluminosilicates. 3130 to 3770 cm\(^{-1}\) owing to O-H stretching which came from the hydrolysis and condensation during the synthesize procedures. At the range brand between 1370 to 1640 cm\(^{-1}\) presents C-H stretching came from -CH\(_3\) groups, which confirms that the carbon-based nanomaterials reinforced T/Q siloxanes are superhydrophobic materials.
3.3.3. Results from Ultra-Small-Angle X-ray Scattering (USAXS)

The results of USAXS reveal that the surfaces of the composites have three different levels, as shown in Figure 3.7, which means the surfaces of all materials are hierarchical, and the surfaces of the four materials are different. The $R_g1$ (the radius of gyration for Level 1) and $R_g2$ (the radius of gyration for Level 2) of MMGO are smaller than other materials, and MMG has the larger ones. Therefore, the pore diameters for MMGO at first and second level are smaller than other materials.

3.3.4. Effects of Different Amounts of Carbon-based Nanomaterials

Figure 3.8 presents indentation load versus depth for superhydrophobic polymers with carbon-based nanomaterials at 0.3 wt. ppt. Although each sample was subject to 100 indent measurements, some indents failed due to improper contacts or excessive cracking, and hence the number of valid measurements is less than 100. Among these loads versus depth curves, the achieved maximum indentation depth varies from ~11 to 15 μm, and most curves terminate at a depth is almost 12 μm, which is less than the preset targeted maximum depth of 15 μm. That is because the maximum load capacity is 625 mN, which limits the achievable maximum indentation depth, basing on the mechanical properties, such as stiffness and hardness of the indented materials. The area with red dash circle is induced by thermal drift (Figure 3.8 a).
Figure 3. 8 Indentation results from carbon-based nanomaterials reinforced T/Q silanes: (a) indentation load versus depth curves for MMG 0.3 wt. ppt; (b) indentation load versus depth curves for MMrGO 0.3 wt. ppt; (c) indentation load versus depth curves for MMWCNTs 0.3 wt. ppt; (d) indentation load versus depth curves for MMGO 0.3 wt. ppt.

Compared with pure SHOIP, Young’s modulus and hardness are largely increased, because pure SHOIP has lots of fractures and is easy to break. Figure 3.9 presents Young’s modulus and hardness changed with indentation depth. There are three different samples tested for nanoindentation test at different amounts of carbon-based nanomaterials, MMG, MMWCNTs, and MMrGO. From Figures 3.9a and 9b, MMG at 3 wt.ppt has the highest Young’s modulus and hardness, but MMG at 9 wt.ppt has the lowest. That means it is not the more amount of graphene, the higher achieved Young’s modulus and hardness. Therefore, graphene does increase the strength of pure SHOIP, but the composite can achieve the highest strength when added to certain
amounts. Obviously, the variations of properties of the three different amounts of added graphene are relatively large, especially at shallow depths, indicating that more amount of graphene can easily aggregate, and the maximum load is 625 mN, so the curves above 625 mN cannot be counted into the validation ones, and less amount of graphene is not enough to improve the strength a lot. Therefore, it is necessary to choose a proper amount of graphene to add.

From Figures 3.9c and 9d, the curves decreased at the shallow depth (less than 400 nm), and then increased with indentation depth, and finally achieved the stable stage (almost from 8000 nm). Young’s modulus and hardness increased with the amount of multi-walled carbon nanotubes, which means MMWCNTs at 3 wt.ppt have much higher Young’s modulus and hardness at any depths than MMWCNTs at 0.3 wt.ppt. The conclusion is that when the amount of multi-walled carbon nanotubes is less than 3 wt.ppt, the more amount, the higher Young’s modulus and hardness, which also indicates the proper amount of MWCNTs is almost same with the graphene.

From Figures 3.9e and 9f, the curves of MMrGO at 0.3 wt.ppt increase at the first stage, and then decrease gradually to the stable stage, but MMrGO at 3 wt.ppt decreases at the first stage, and then increases gradually to the stable stage. The difference may be caused by surface elastic and side effects, and also maybe the more amount of rGO, there are more aggregation happened at small scale. Young’s modulus and hardness of MMrGO at 3 wt.ppt are almost the same with MMrGO at 0.3 wt.ppt at the depth of 15 μm, but for other depths (1-14 μm), Young’s modulus and hardness of MMrGO at 0.3 wt.ppt are higher than MMrGO at 3 wt.ppt. Obviously, for MMrGO, the proper amount of rGO is 0.3 wt.ppt, therefore, there is no need to add more to improve the strength.
Figure 3.9 Nanoindentation results for different samples: (a) Young’s modulus with indentation depth for MMG at different amounts of graphene; (b) Hardness with indentation depth for MMG at different amounts of graphene; (c) Young’s modulus with indentation depth for MMCNTs at different amounts of multi-walled carbon nanotubes; (d) Hardness with indentation depth for MMCNTs at different amounts of multi-walled carbon nanotubes; (e) Young’s modulus with indentation depth for MMrGO at different amounts of rGO; (f) Hardness with indentation depth for MMrGO at different amounts of rGO.
3.3.5. Effect of Different Kinds of Carbon-based Nanomaterials

Figure 3.10 shows the mechanical properties of the four samples at the same amount of added carbon-based nanomaterials. MMrGO has the highest Young’s modulus and Hardness than the other three composites and the curve of MMGO is the second which is very close to the MMrGO, but the MMWCNTs have the lowest, that means at the same conditions, rGO or GO is the best material to improve the mechanical properties among the carbon-based nanomaterials. All the curves except MMWCNTs in Figure 3.10a displayed similar behavior at the same amount of 0.3 wt.ppt. They dramatically decreased and then came back for a little bit at the initial stage (i.e., 0-1 μm), and gradually decreased to a stable stage when the penetration depth increased. For MMWNCTs’, the curve dramatically decreased and tended to a stable stage when the penetration depth increased. The MMrGO has the highest Young’s modulus at the depth of 15 μm when compared to other materials, and the Young’s modulus is almost up to 7 GPa. Also, these curves indicate even at the same amount of carbon-based nanomaterials, the strength is different, which means the mechanisms are different. The mechanisms will be discussed later.

In Figure 3.10b, all curves presented the hardness changes with indentation depth, the curves dramatically decreased at the initial stage and then came back at 0-1 μm, and gradually decreased to a stable stage. The hardnesses of MMGO and MMrGO are most the same at the depth of 15 μm, but MMrGO has a greater hardness than MMGO at the other depths.

Figure 3. 10 Nanoindentation results for different samples at the same amount of adding carbon-based nanomaterials: (a) Young’s modulus with indentation depth for carbon-based nanomaterials added with 0.3 wt.ppt; (b) Hardness with indentation depth for carbon-based nanomaterials added with 0.3 wt.ppt.
3.3.6. Wear Testing

Figure 3.11b shows the height difference increased with the number of cycles, which indicates the abrasion resistance for each material. Learned from this figure, SHOIP is the easiest material to be abraded because it nearly has no strength, but MMGO and MMrGO at 0.3 wt.ppt are the hardest to wear. Except for SHOIP, the height of MMWCNTs is increased the most compared with other composites. These results are mostly in agreement with the results of the nanoindentation test because there isn’t too much difference between MMGO and MMrGO at 0.3 wt.ppt.

Figure 3.11 Wear testing: (a) Schematic of wear testing; (b) height difference increased with the number of cycles.

3.3.7. Surface Morphology and Element Analysis

Figure 3.12 presents the SEM images of all samples with 0.3 wt.ppt carbon-based nanomaterials reinforced T/Q silanes, the surfaces of the composites are hierarchical, and the hierarchical surface roughness is induced by the synthesized aluminosilicones and incorporated in the methyl end groups, which confirmed by the previous results. However, except for the hierarchical surfaces, there are lots of fibers can be observed on the surfaces. From Figures 3.12a
and 12b, MMG composite with 0.3 wt.ppt of graphene, besides the hierarchical surface and some fibers, there are lots of graphene sheets that can be observed, because graphene is hard to completely disperse, so there are still some aggregations happened even cured under 75°C. The observe rod-like features on the surfaces of the composites (as shown in Figure 3.12a), and the rod-like features with a diameter of 300 ~ 500 nm on the surface of MMG, but the size of graphene used in this paper is of 25 μm width and 6~8 nm thickness. Therefore, it is reasonable to assume that these rod-like features are rolled up with themselves and/or aluminosilicate. That means carbon-based nanomaterials were rolled up inside, and then covered with aluminosilicones. To confirm the assumption, EDS was used to do the elemental analysis (as presented in Figure 3.13b). The elements including Si, Al, Na, O, and C can be tested, which can confirm the assumption that the fibers consisted of aluminosilicates and graphene sheets, which means the rod-like features were rolled up with themselves and with aluminosilicones. The mechanisms will be discussed later.

Figures 3.12c to 12h show the surface of MMrGO, MMGO, and MMWCNTs, and there are also some rod-like features can be observed. When observed the fibers at 1 μm, the fibers are not empty, and the ends are cover with stuff from Figure 3.12 d. According to Figures 12c to 11h, there are also five elements can be tested, therefore, the fibers are not only carbon-based nanomaterials, but also include aluminosilicate.
3.4. DISCUSSION

Based on the above results, it is well known that there are lots of fibers on the surfaces of all composites, except for the hierarchical surfaces and some aggregation because of van der Walls forces. As discussed above, these rod-like features are rolled up with themselves or with aluminosilicones with the help of ultrasonic waves. However, the composites with different carbon-based nanomaterials have different mechanisms based on their chemical and physical structures.

The mechanisms of graphene to strength the pure T/Q siloxane as follows: (1) graphene as a nanomaterial can bridge the fractures in the matrix and increase the strength of materials, and it also has very high strength, so it can improve lots of strength of the composite; (2) based on Figures 3.13a and 13b, the rod-like features include Si, Al, Na, O, and C elements. Si, Al, Na, and O come from aluminosilicones, and Na and O may also come from sodium hydroxide or sodium carbonate after reacting with CO₂ when sodium hydroxide exposed to the air. C comes from carbon-based nanomaterials or organic backbones (like -CH₂). However, there are no fibers on the surface of pure SHOIP even cured under ultrasonic waves, so C comes from graphene. Because of the curing condition, the ultrasonic waves were introduced to disperse the nanomaterials, and ultrasonic bath with 42 kHz sonic radiation is easy to break chemical bonds, such as C-C bonds, and also because ultrasonic wave induced cavitation and the bubble was created, grown, and collapsed in the sonochemistry of the slurry (Gedanken, 2004a). Therefore, ultrasonic irradiation in liquid dispersion can induce graphene sheets to deform, damage, and guide the folding of graphene sheets in several sizes and shapes (Guittonneau et al., 2010). When the chemical bonds were damaged with sonication, the graphene sheets would roll up with themselves, and with the functional groups resulted in carbon-based nanomaterials rolled up with aluminosilicones.

The mechanisms of rGO to improve the strength of the pure T/Q siloxane are as follows: (1) it also works as nanomaterials to bridge the fractures in the matrix and increase the strength of materials because of its own superior mechanical properties; (2) the chemical bond can be broken
with ultrasonic waves, and rGO can be rolled up with themselves and also rolled up with aluminosilicones; (3) from Figure 3.5b, there are some holes on the structure of rGO, which means the aluminosilicones can penetrate through the holes of rGO and tangle with rGO under ultrasonic irradiation, which is physical interaction.

The mechanisms of GO to improve the strength of the pure T/Q siloxane are the same with rGO, except for the last one. The last mechanism for GO is the chemical reaction. From Figure 3.5a, there are lots of functional groups on the structure of GO, such as hydrogen, and carboxyl groups, which are easily to react with other materials, so the functional groups of GO interact with aluminosilicones and are rolled up with the help of ultrasonic waves.

The mechanisms of strengthening pure SHOIP with MMWCNTs are different with graphene, rGO and GO. That is because MMWCNTs just physically tangle with aluminosilicones and insert into the pores and fractures of the matrix as bridges to reinforce the strength of pure SHOIP, which can be indicated with SEM with EDS (as shown in Figures 3.13g and 13h). The amounts of carbon and oxygen are much higher than other elements, which means small amount of aluminosilicons attached on the surface of MMWCNTs, and MMWCNTs as bridges to connect the fractures and pores in the matrix. The rod-like features on the surface of MMWCNTs are mostly the part of MWCNTs can also be indicated with the size of rod-like features, because the diameters of fibers are less than 100 nm, but the size of MWCNTs used in this paper is greater of 5 μm length and between 60 ~100 nm diameter. From the results of EDS (as shown in Figure 3.13h) the rod-like features are mostly the MWCNTs, but there are some organic or inorganic materials stuck on the surface of nanotubes.

As the above discussed, different carbon-based nanomaterials have different mechanisms to improve the strength of the pure T/Q siloxane. carbon-based nanomaterials can fill the mesoporous materials. Therefore, the fractures can be bridged by the nanomaterials and the strength can be increased with the fillings. Therefore, in wear testing, the anti-abrasion property could be also attributed to the fiber-entangled porous structure of the micro-size particles (as shown in Figure 3.13). The abrasion test indeed partially removes entangled nanofibers at the top surface, but the substrate is still consisting of “similar” hierarchical nano/microstructures. That is, the remaining structure resembled the original surface prior to abrasion. Therefore, the
combination of chemical bonding and physical tangling can achieve superior anti-abrasion properties as well.

From Figures 3.9e and 9f, the composites with rGO at 0.3 wt.ppt and 3 wt.ppt have the same Young’s modulus and Hardness at 15 µm. There are two reasons for these. First, rGO is an immensely strong material which contributes to the increase in its strength, therefore, 0.3 wt.ppt is already the proper amount to add no matter as nanomaterial or tangled with other stuff. Second, as a nanomaterial is added into mesoporous materials with ultrasonic waves (Landau et al., 2001), the nanoparticles can be deposited as a smooth layer on the inner mesopores wall without blocking them, but if added more rGO, it will not help to improve strength anymore.

There are several reasons to explain why GO and rGO can increase the most strength of pure SHOIP in Figure 3.10 and Figure 3.11b: one is GO and rGO has good dispersibility in the solvent which makes as a nanomaterial that can fill the mesoporous materials and work as bridges to connect the fractures of matrix materials very well; the other one is GO has lots of hydroxyl and carboxyl groups (as discussed above), which can interact with aluminosilicones, that means GO and aluminosilicones can be rolled up with the help of ultrasonic waves after chemical reactions, but for rGO, it has lots of holes on the structure, so the other stuff is easy to penetrate and tangled with rGO.

From Figure 3.10., MMWCNTs has the lowest Young’s modulus and hardness than other composites at the same amount of materials, but Young’s modulus and hardness are still greater than pure SHOIP in Figure 3.11b. MWCNTs can be inserted into the mesopores as nanomaterials with the help of ultrasonic waves. That means multi-walled carbon nanotubes not only fill the pores but also bridge the cracks, which increases the strength of the composite. This is why for graphene and MWCNTs, 3 wt.ppt is the proper amount of nanomaterials to add, but 0.3 wt.ppt of rGO is the appropriate amount to reinforce the pure T/Q silanes.
Figure 3. Elemental analysis for carbon-based nanomaterials: (a) SEM micrograph of graphene sheets tangle with aluminosilicones at 3 μm; (b) elemental spectrum of MMG at 0.3 wt.ppt; (c) SEM micrograph of reduced graphene oxide sheets tangle with aluminosilicones at 2 μm; (d) elemental spectrum of MMrGO at 0.3 wt.ppt; (e) SEM micrograph of graphene oxide sheets tangle with aluminosilicones at 4 μm; (f) elemental spectrum of MMGO at 0.3 wt.ppt; (g) SEM micrograph of multi-walled carbon nanotubes tangle with aluminosilicones at 400 nm; (h) elemental spectrum of MMWCNTs at 0.3 wt. ppt.
3.5. CONCLUSIONS

The improved bulk superhydrophobic polymers with carbon-based nanomaterials exhibit higher strength and mechanical abrasion, and the Young’s modulus and hardness can be achieved up to 7 GPa and 0.15 GPa at depth of 15 μm, respectively. The mechanisms of reinforcements are different for various carbon-based nanomaterials. Each carbon-nanomaterial has different mechanisms to reinforce the strength of polymers based on its own chemical and physical structure.

The mechanisms behind graphene to reinforce superhydrophobic polymer are two ways: the first is graphene as nanomaterials can refill the pores and fractures of matrix; the second one is graphene can be damaged with ultrasonic wave, and the broken C-C bond can be physically tangled with aluminosilicones and formed fibers to improve the strength.

There are three ways for rGO to reinforcement: the first and the second ways are the same with graphene; but the third one is the structure of rGO, so the aluminosilicones can penetrate the holes on the structure of rGO, and then physically tangled with each other.

GO also has three ways to reinforce the superhydrophobic polymer, and the first two ways are the same with the rGO. The third mechanism is there are lots of functional groups on the structure of GO, and the functional groups can react with aluminosilicones, such as hydrolysis and condensation, and then chemically tangled with each other.

MMWCNTs just have one way to improve the strength of the superhydrophobic polymer, which is as a nanomaterial to refill and bridge the pores and fractures of the matrix, which helps the load-transfer in case of tension.

Therefore, compared to other carbon-based nanomaterials, GO and rGO present the best properties and mechanisms to reinforce the bulk superhydrophobic composites.
4. MICROSCALE DISPERSION AND MACROSACLE DISTRIBUTION OF REINFORCING GRAPHENE IN A SUPERHYDROPHOBIC SILOXANE

Three-dimensional voluminous superhydrophobic materials are usually characterized by low fracture toughness and extremely low strength due to the low surface energy on internal surfaces and hence require reinforcements for viable practical applications. This paper presents an experimental study on a graphene-reinforced superhydrophobic siloxane, emphasizing the effects of microscale dispersion and macroscale distribution of reinforcing graphene on the homogeneity and strength of the composite. The sol-gel synthesis of the composite involved alkali activation of metakaolin and hydrolysis of alkoxyisilane, followed by mixing graphene into the precursor sol prior to co-condensation at atmospheric pressure. To promote uniform dispersion and distribution of graphene nanoplatelets, three processing methods were adopted: (1) ultrasonication to disperse graphene in the sol; (2) accelerated co-condensation at elevated temperatures (i.e., 50 and 75°C) to prevent graphene from floating and re-aggregation; (3) varying the sol’s viscosity to control graphene movement. Nanoindentation, porosimetry, and unconfined compression were performed to characterize the cured composite. Results show that adding only 0.9 wt.% graphene increases the strength of the superhydrophobic composites from ~0 to ~10-33 MPa. However, graphene tends to re-aggregate and float upward in the sol, leading to its heterogeneous distribution at different scales in the cured composite. On the other hand, despite its functionality of improving microscale dispersion, ultrasonication detrimentally decreases the composite’s strength due to acoustic cavitation. Similarly, although curing at elevated temperatures accelerates the condensation and hence results in a more uniform distribution of graphene, it also induces thermal cavitation and bubble formation. The underlying mechanism is that the thresholds for both acoustic and thermal cavitations are significantly reduced by superhydrophobicity. Therefore, caution should be taken in applying proven sol-gel processing techniques developed for hydrophilic materials to superhydrophobic counterparts.
Figure 4. 1 Graphical abstract
4.1 INTRODUCTION

Two-dimensional (2D) superhydrophobic surfaces, traditionally defined by a static water contact angle (WCA) of >150°, are characterized by two peculiar physical and chemical properties: the former refers to the multiscale, usually hierarchical, surface roughness or other surface microstructures (e.g., doubly reentrant cavities) (Domingues et al., 2018; L. Gao & McCarthy, 2006; T. Liu & Kim, 2014), while the latter requires the surface to possess nonpolar, low-energy moieties (e.g., waxy coating on lotus leaf, functional groups such as -CH₃, -CF₃, and -SiO₄) that repel water (Cheng et al., 2013; Nishino et al., 1999; Quéré & Reyssat, 2008). In fact, the maximum static WCA for an ideally smooth surface with the current technology-achievable minimum chemical surface energy via fluorinated carbon chains (i.e., -(CF₂)n-CF₃) is ~ 119-120° (D. Wang et al., 2020b; Webb et al., 2014b), but cannot be >150°, further demonstrating the contribution of surface roughness and multiscale structures to superhydrophobicity. These two features of a superhydrophobic surface render it highly water-repellent and non-adhesive to most hydrophilic materials, obviously due to its extremely low intrinsic surface energy and small contact areas resulting from the highly rough surface (Blossey, 2003; Packham, 2003; Verho et al., 2011).

On the other hand, 3D voluminous superhydrophobic materials feature a WCA of >150° on the majority, if not virtually any, of cross-sectional internal surfaces through the bulk materials (Das et al., 2017; Simpson et al., 2015b). According to the aforementioned two requirements for a surface with a WCA of >150°, the fractured internal surface of a 3D superhydrophobic material must also possess multiscale surface roughness, which is usually achieved by a microporous structure that, upon fracture, makes up the rough texture. On the other hand, a fractured surface is usually occupied by hydrophilic moieties (e.g., -OH for most oxides such as hematite and silica, and even clay mineral edge surfaces) due to the broken bonds (X. Liu et al., 2013; Pecini & Avena, 2013; Tournassat et al., 2003). According to the Wenzel model (Robert N. Wenzel, n.d.), the surface roughness can decrease the WCA of a hydrophilic surface but increase it for a hydrophobic surface. As such, the low chemical energy of a fractured surface must be derived from the nonpolar functional groups pre-existing on the internal surface of the micropores, which can partially compensate the hydrophilicity of the broken bonds on the fractured surface. Accordingly, a 3D superhydrophobic material usually exhibits very low strength and fracture roughness because an internal cross-sectional fracture surface always has a low surface energy, or fracture always occur
on an internal surface with the lowest surface energy. Such an inherent drawback limits the practical, widespread applications of 3D superhydrophobic materials. To overcome this deficiency, internal reinforcements that can be mixed or added to the bulk matrix are desired and relevant technologies should be developed.

Much work has demonstrated that graphene nanoplatelets, carbon nanotubes (CNT), and other nanofibers are ideal nanoscale reinforcing fillers for a plethora of composites, such as cements and concretes (D. Lu & Zhong, 2022; Sheikh et al., 2021), polymers (Araby et al., 2021; Yan et al., 2018), elastomers (Araby et al., 2015), and even metals (Fritea et al., 2021). Nanomaterials can ideally suppress and intervene the very first nucleation of nanoscale cracks and further restrain the growth and propagation of microscale cracks by functioning as bridges. In fact, carbon-based nanomaterials, such as graphene and CNT, are widely used to reinforce and functionalize cementitious materials, because of their superior mechanical performance, lightweight, and unique structure. For example, multilayer graphene was added to ordinary Portland cement (OPC) to improve its strength, and the compressive strength and elastic modulus of the resulting composites increased by 54 and 50%, respectively (Sun et al., 2017). Moreover, 2D nanographene is particularly a promising filler for high-performance multifunctional nanocomposites because of its superior mechanical, electrical, thermal, and optical properties. It can improve the mechanical properties such as tensile strength and Young’s modulus of polymers via effective interfacial stress transfer (Arash et al., 2014; Coleman et al., 2006). In theory, the tensile strength and Young’s modulus of graphene can reach 130 GPa and 1.0 TPa, respectively (C. Lee et al., 2008b), and its specific surface area is extremely high, up to 2,360 m²/g, enabling ample interfacial interactions with the host material. In addition, it can also effectively toughen fragile polymers by increasing the crack propagation path in the nanocomposite.

It is well known that complete dispersion of nanomaterials as reinforcing fillers in the nanocomposite’s host matrix (e.g., cementitious materials such as OPC and geopolymers, polymers) is highly challenging or even unachievable, because of the dominance of surface forces of the nanomaterials over gravity and other forces. For instance, the presence of relatively strong van der Waals forces (e.g., 5.9 kJ/mol) between graphene nanoplatelets can usually induce aggregation or make complete dispersion infeasible (Sun et al., 2021). Strengthening the interfacial interactions between graphene and the host matrix is essential for improving its dispersion and
reinforcing functionality (Liu et al., 2018). As such, much effort has been devoted to developing effective and efficient dispersion techniques for nanomaterials. To date, proven effective chemical surface treatments or modifications include, for example, acid treatment (Li et al., 2004), oxidation with heating (George et al., 2008), ozone treatment (Leconte et al., 2010), and surface silanization (Wan et al., 2014). The difficulty of nanomaterial’s dispersion also partly arises from the surface energy or hydrophobicity, since a hydrophobic reinforcing filler (e.g., CNT, some polymer fibers) is usually not compatible with a hydrophilic matrix or vice versa. For instance, hydrophobic attractions between two hydrophobic surfaces or nanoparticles prevent their separation and dispersion (Meyer et al., 2006; J. Zhang & Zeng, 2021). On the other hand, proven physical or mechanical dispersion techniques are also available. For example, ultrasonication is effective in facilitating the dispersion of reinforcing nanofillers in a liquid or semi-liquid matrix (Calvaresi et al., 2013), and has been widely used for dispersing an array of various fillers (Gedanken, 2004b). However, an inevitable side, probably negative influence of ultrasound dispersion is the promotion of bubble nucleation, growth, and eventually implosion, which can be collectively termed as cavitation (Bussonnière et al., 2020; Rezk et al., 2021; D. Yu et al., 2012), owing to the introduction of more defect-like pores into the bulk materials that have then reduced density. Such a negative effect of cavitation-assisted dispersion of reinforcing nanofillers on the strength development has not been widely observed nor well documented in the literature, especially for hydrophobic or superhydrophobic materials.

Cavitation, a process of bubble nucleation, growth, and implosion, has been well-studied in several disciplines such as physics, colloid and interface science, and sonochemistry, among others (Barney et al., 2020; Bremond et al., 2005; Caupin & Herbert, 2006; Hasan & Iyengar, 1963; Luo et al., 2021; Rastogi et al., n.d.; Scherer & Smith, 1995; Shen et al., 2021). Several factors can promote cavitation, such as heterogeneous interfaces, temperature, surface energy, and ultrasound wave (Arrojo & Benito, 2008; Belova et al., 2011; Christenson & Claesson, 1988; Shchukin et al., 2011). In particular, compared with a smooth or hydrophilic surface, hydrophobic surfaces can lower the threshold of bubble nucleation and cavitation (Aghdam et al., 2019; Belova et al., 2011; Christenson & Claesson, 1988; Jin et al., 2016a; Luo et al., 2021). More importantly, for the superhydrophobic surface with multiscale surface roughness or microstructure, small air bubbles or pockets may pre-exist in the small cavities on the rough surface and hence can significantly
augment bubble growth and implosion by lowering the cavitation threshold. In other words, cavitation may be more pronounced on a superhydrophobic surface and even become highly severe or dramatic within a 3D superhydrophobic, porous materials.

Recently, a new 3D superhydrophobic siloxane has been synthesized by the authors via a sol-gel process consisting of alkali activation of amorphous aluminosilicates (e.g., metakaolin, fly ash, furnace slag), hydrolysis of alkoxy silanes, and hybrid co-condensation of inorganic silanols (Si(OH)₄), inorganic Na-aluminols (NaAl(OH)₃), and organic methyl silanols (H₃C-Si(OH)₃), resulting in an aluminum-bearing TQ siloxane, where T and Q represent the tri- and tetra-functional siloxane structural units respectively (i.e., T = CH₃SiO₃/2 unit, Q = SiO₄/2 unit). Because of its voluminous superhydrophobicity, this material is highly porous and has a very low strength and fracture toughness. In fact, it was observed that the bulk material self-cracked and fractured automatically during the curing and drying process, making practical applications impossible. Therefore, hydrophilic graphene was chosen to reinforce and strengthen this material. Preliminary experiments found some abnormal phenomena that contradicted the widely accepted perception, such as increasing curing temperature results in a stronger material, and ultrasonication can achieve a more uniform distribution of graphene. As such, more effort was made to uncover the underlying mechanisms for the observed abnormal behavior. This paper presents an experimental study on the microscale dispersion and macroscale distribution of reinforcing graphene in the 3D superhydrophobic TQ siloxane. To achieve improved dispersion and uniform distribution of graphene nanofillers within the sol-gel matrix, and hence optimized mechanical performance, ultrasonication, high-temperature curing, and altering the precursor sol’s viscosity were investigated. The resulting composites still maintain a WCA of >150°, but with a significantly improved macroscale compressive strength of up to ~34 MPa, well exceeding those of OPC. One of the key findings is that increasing curing temperature surprisingly leads to a weaker superhydrophobic composite.
4.2. MATERIALS AND METHODS

4.2.1 Materials

The as-received dry powder of PowerPozz™ metakaolin (MK, Al₂O₃·2SiO₂, Advanced Cement Technologies, LLC., WA, USA) was used as the raw material for alkali activation, and its particle size distribution measured by the relevant standard method and chemical composition are shown in Table 3.1. The alkaline activator consisted of a mixture of sodium silicate solution (Na₂O·SiO₂·5H₂O, Ricca Chemical Co., TX, USA) and sodium hydroxide (NaOH, Fisher Scientific, Inc., USA), whose chemical compositions are also compared in Table 4.1. The former was a technical-grade solution with a 40°-42° Baumé (i.e., an average density of 1.4 g/cm³ or specific gravity of 1.38 to 1.42 at 25°C) and pH 11.2, while the latter was white solid pellets with a ≥98% purity quotient. A trifunctional alkoxy silane (i.e., T silane), nitrogen-flushed methyltrimethoxysilane (MTMS, CH₃Si(OCH₃)₃, 97%, Acros Organics, Inc., NJ, USA), was selected as the hydrolyzable agent to lower the surface energy via introducing the organic -SiCH₃ moiety to the siloxane. Graphene nanoplatelet (Strem Chemicals, Inc., MA, USA) with a nominal thickness and length of 6-8 nm and ~25 µm respectively was selected as the nanofiller to strengthen the superhydrophobic TQ siloxane.

4.2.2 Synthesis of Graphene-reinforced Siloxanes

The general process for synthesis of the studied siloxane consisted of alkali activation of the amorphous aluminosilicate (i.e., MK), hydrolysis of the T silane MTMS, and hybrid co-condensation of alkali-activated inorganic tetrafunctional (Q) silanols (Si(OH)₄) and Na-aluminols (NaAl(OH)₄) as well as hydrolysis-generated, trifunctional (T) organic methyl silanols (H₃CSi(OH)₃). The pure siloxane (i.e., without graphene as the nanofiller) was pre-designed to have a fixed nominal Si/Al, Na/Al, and T/Q molar ratio of 1.7, 1.0, and 0.0625, respectively, and the silicon in the Si/Al ratio included the Si from both the trifunctional (T, RSiO₃/₂, where R is an organic radical) and tetrafunctional (Q, SiO₄/₂) structural units. Such a TQ siloxane was superhydrophobic due to the grafting of methyl (i.e., -CH₃) groups into the siloxane at its end or surface and hence had little strength or fracture toughness, as indicated by the fact that the
completely cured sample could be crushed with finger pressure or self-crack naturally during curing and drying. Therefore, to improve its mechanical properties, graphene nanoplatelets were used as the reinforcing filler, which was added to the precursor sol after alkali activation and hydrolysis, but prior to condensation or hardening and drying.

The synthesis procedure started with preparing the alkaline activator solution (Figure 4.2) by dissolving NaOH pellets in deionized water, followed by adding the desired amount of sodium silicate solution. Upon complete cooling of the mixture to the room temperature, MK powder was added to the activator solution, followed by continuous mixing for 25-30 min to achieve complete MK dissolution (i.e., alkali activation reaction), resulting in a viscous homogeneous precursor sol containing activated silanols and Na-aluminols. Then the desired amount (i.e., a pre-designed T/Q ratio of 0.0625) of MTMS was added dropwise via a pipet to the sol while it was being continuously stirred to facilitate the uniform distribution of the MTMS. This step usually took 20-30 min to finish and was followed by at least 15-minute continuous stirring to promote the breakdown and hydrolysis of the initially immiscible MTMS droplets. Finally, graphene nanoplatelets were added to the above sol at a concentration of 0.9 wt.%, followed by 25 min ultrasonication for better dispersion using an FS60 bath-type ultrasonic cleaner (Fisher Scientific, Inc., USA) that generated 100 W and 42 kHz ultrasound waves. As graphene powder has a black color, the final composite precursor sol was a black homogeneous slurry. Since synthesis of the TQ siloxane involved adding water and liquid T silane as well as generating highly volatile methanol, and curing and drying led to the loss of water and methanol, it makes little sense to use the total mass of all raw source materials (i.e., including water) used in the synthesis as the basis to calculate the graphene content. Instead, the graphene content (i.e., 0.9 wt.%) was defined as the ratio (e.g., expressed as a percentage) of the mass of pure graphene to that of the completely cured and dried TQ siloxane.
The above homogenized precursor slurry was then cast into half-split cylindrical high-density polyethylene molds with an inner diameter and height of 25.4 and 63.5 mm respectively, which were coated with a thin layer of vacuum grease on the inner surface to facilitate subsequent demolding (Figure 4.3). The slurry samples in the molds were initially cured in an oven at elevated temperatures (i.e., 50 and 75°C) or the atmosphere at room temperature (i.e., 25°C) for 7 days or until they became stiff enough for handling, followed by demolding and further curing in open atmosphere for at least additional 7 days or until they were dried completely, as indicated by no further change in their mass.
Figure 4. 3 Molds for curing samples: (a) a completely disassembled mold showing the two split half cylinders and two end caps; (b) a fully assembled mold with a cured sample; (c) self-cracking sample with no graphene; (d) water droplets on the surface of sample without graphene.

Table 4.1 summarizes all the different samples prepared in this study, each with its specific designation (i.e., sample ID). For comparison, a pure siloxane without graphene (i.e., Sample T25-0G) was also synthesized with the same parameters (i.e., Si/Al, Na/Al, and T/Q molar ratios of 1.7, 1.0, and 0.0625, respectively) and cured at 25°C. Since no graphene was used, the precursor slurry was not subject to ultrasonication dispersion or high-temperature curing. Also, once demolded, the cylindrical sample experienced self-cracking in the subsequent air-curing (Figures 4.3c and 3d). In this table, all other samples were prepared at a fixed graphene content of 0.9 wt.%, but some
curing conditions were varied, including three different curing temperatures (i.e., 25, 50, and 75°C) for different condensation or hardening reaction rates, whether or not using 25 min ultrasonication for better dispersion of graphene, and three different water/solid ratios (i.e., 28.23, 40.33, and 52.42 wt.%) for different densities and viscosities of the precursor sol. As discussed later, these three parameters probably dominantly control the dispersion-aggregation and distribution-flotation of graphene nanofillers in the precursor sol. Further noteworthy is that the 40.33 wt.% water/solid ratio corresponded to a H₂O/Na₂O molar ratio of 17.5.

Table 4.1 Samples with different curing conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Graphene content (wt.%)</th>
<th>Curing Temperature (℃)</th>
<th>Ultrasound dispersion (Y/N)</th>
<th>Water/solid ratio* (wt.%)</th>
<th>Bulk density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T25-0G</td>
<td>0</td>
<td>25</td>
<td>No</td>
<td>40.33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T25-U</td>
<td>0.9</td>
<td>25</td>
<td>No</td>
<td>40.33</td>
<td>1.530</td>
<td>33.3</td>
</tr>
<tr>
<td>T25+U</td>
<td>0.9</td>
<td>25</td>
<td>Yes</td>
<td>40.33</td>
<td>1.454</td>
<td>37.6</td>
</tr>
<tr>
<td>T50+U</td>
<td>0.9</td>
<td>50</td>
<td>Yes</td>
<td>40.33</td>
<td>1.357</td>
<td>40.5</td>
</tr>
<tr>
<td>T75+U</td>
<td>0.9</td>
<td>75</td>
<td>Yes</td>
<td>40.33</td>
<td>1.350</td>
<td>40.7</td>
</tr>
<tr>
<td>T75+U+W</td>
<td>0.9</td>
<td>75</td>
<td>Yes</td>
<td>52.42</td>
<td>1.261</td>
<td>42.5</td>
</tr>
<tr>
<td>T75+U-W</td>
<td>0.9</td>
<td>75</td>
<td>Yes</td>
<td>28.23</td>
<td>1.445</td>
<td>37.4</td>
</tr>
</tbody>
</table>

*Water/solid ratio is defined as the mass of water to that of the slurry mixture but excluding water.

4.2.3 Sample Preparation

To characterize the macroscopic spatial distribution of the graphene nanofiller within the siloxane, the above completely cured and dried cylindrical samples were divided by a carbide-tipped saw blade into three horizontally equal sections, namely Top, Middle, and Bottom (Figure 4.4a). For each of the three sections, a thin disk of ~5 and 25.4 mm in thickness and diameter respectively was trimmed for subsequent nanoindentation testing (Figure 4.4b). The residual part was then further trimmed into two cubes of ~10 × 10 × 10 mm (Figure 4.4c), which were manually polished using a P1000 (i.e., grit size 18 μm) Buehler’s CarbiMet (Buehler Inc., IL, USA) silicon
carbide grinding paper. During polishing, each set of two opposite surfaces were frequently checked and measured to ensure they were parallel to each other. One of these cubes was used for unconfined compression testing, and the other for porosimetry.

The thin disks used for nanoindentation testing required fine polishing. After preliminary manual polishing, each disk was first mounted onto a cylindrical aluminum puck of 25.4 mm in diameter (i.e., a standard sample stage for the G200 nanoindenter used in this study) with the Crystalbond 509 amber resin (Aremco Products, Inc., NY, USA) as the mounting adhesive that

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**Figure 4.** The samples for tests: (a) the schematic of MMG at three different layers without curing; (b) a polished thin disk for nanoindentation testing obtained from each layer; (c) sample for unconfined compression obtained from each layer; (d) sample for unconfined compression obtained from (c).
melts at 130°C and hardens upon cooling. Then such mounted disk specimen was successively polished in a MetaServ 250 polisher (Buehler Inc., Lake Bluff, IL, USA) by firstly abrasive Buehler’s CarbiMet and MicroCut silicon carbide grinding papers with grit sizes decreasing successively from P180 to P4000 (i.e., P180, P280, P400, P800, P1000, P1200, P1500, P2500, and P4000 with the equivalent grit sizes of 78, 52, 35, 22, 18, 15, 13, 8, and 5 μm, respectively) and secondly alumina lapping films with grit sizes decreasing from 3.0, 1.0, to 0.3 μm to acquire a smooth and flat surface. Based on prior experience, the root-mean-square roughness ($R_{\text{rms}}$) of such polished rock specimens measured by atomic force microscopy is < 150 nm. Also, each time when changing the abrasive paper, filtered pressurized air was used to remove the polishing debris and dust from the polished surface. All polishing used no water or oil, and the slowest rotation speed and frequent pause to avoid generating excessive heat that might damage the samples.

4.2.4 Water Contact Angle Measurements

To examine the hydrophobicity, static water contact angles (WCA) were measured in a Dataphysics OCA 15EC contact angle measurement system. A 10 μL water drop was dispensed by a syringe needle and static images immediately captured and then analyzed. Both finely-ground powder and block samples were tested. The former was obtained by hand-grinding a piece of fractured sample in a mortar and pestle to pass all material through a #625 mesh (i.e., an opening size of 20 μm), followed by light compaction to form a smooth and flat surface for WCA measurements. The latter were cut from the original cylindrical samples, followed by manual polishing with sandpapers to have a relatively flat surface. All measurements were performed at room temperature and atmospheric pressure. In addition, to check the 3D voluminous superhydrophobicity of the pure siloxane and its composites, simple visual checking was conducted by observing the formation and quick sliding runoff of nearly spherical water droplets dispensed via a syringe needle on many freshly fractured, differently oriented cross-sectional surfaces.
4.2.5 Porosimetry

Mercury intrusion porosimetry (MIP) was also performed in an AutoPore IV 9500 (Micromeritics Instrument Corporation, GA, USA) porosimeter with injection pressures of up to 60,000 psia to characterize the pore size distribution (PSD), total porosity, and bulk density of all five samples containing graphene reinforcements. Because the pure siloxane sample had numerous cracks after complete curing and had little strength, which made trimming a cube sample impossible, no MIP was performed on Sample T25-0G (Table 4.1). For the 5 samples with graphene reinforcements, the small cubes of ~1.0 × 1.0 × 1.0 cm trimmed from the different layers of original cylindrical samples, as described in Section 2.3 (Figure 4.4c), were used for the MIP measurements.

4.2.6 Nanoindentation Testing

Nanoindentation testing was conducted in a Keysight G200 nanoindenter (Keysight Technologies, Inc., Santa Rosa, CA, USA) equipped with a customized Berkovich diamond tip of < 20 nm in tip radius and ~ 25 μm in effective depth and an electromagnetic load sensor of 625 mN in capacity. The load was applied at a constant indentation strain rate \( \dot{h}/h \) (where \( h \) is the indentation depth) of 0.05 s\(^{-1} \) under the continuous stiffness measurement (CSM) mode with an acceptable thermal drift rate of < 0.05 nm/s. The target maximum indentation depth \( h_{\text{max}} \) for all measurements was set to 15 μm. However, depending on the tested material’s properties, an indent might stop prior to reaching the \( h_{\text{max}} \) of 15 μm if the load exceeded the load sensor’s capacity (i.e., 625 mN). The reason for selecting such a large maximum indentation depth was four-fold: (1) to eliminate the potential negative interference of surface roughness as well as micropores in the samples with the measurement; (2) to characterize the depth-dependent variability of the tested samples; (3) to account for the possible localized effects of the graphene nanoplatelets of ~25 μm in nominal length; and (4) to enable the extraction of the mesoscale or macroscale properties of the samples, at least for the elasticity, since the elastically-deformed zone beneath the indenter tip is roughly ~ 10\( h_{\text{max}} \) (i.e., a zone with a diameter of ~ 150 μm should encompass enough graphene nanoplatelets as well as some microstructure features such as micropores of the tested samples). The CSM loading mode involved the superposition of a harmonic oscillation of 2 nm and 45 Hz
in amplitude and frequency respectively over the monotonic, constant indentation-strain-rate loading process. Upon reaching the maximum depth, the load was held constant for 60 s, followed by monotonic unloading at a constant loading rate that was the same as the one at the maximum load $F_{\text{max}}$. When the load decreased to 10% of $F_{\text{max}}$, unloading was stopped and the load was held constant for 10 s to record the thermal drift, followed by complete unloading.

For each sample, a total of 100 indents, arranged in a $10 \times 10$ grid with a spacing of 300 μm (i.e., $20 \times h_{\text{max}}$) between two adjacent indents to prevent negative interference from each other (Sudharshan Phani & Oliver, 2019), were obtained. Such a grid covered an area of more than 2,700 × 2,700 μm². In general, the indentation load and depth were recorded with time, and the data analyzed by the widely accepted Oliver and Pharr method (Oliver & Pharr, 1992) to derive the samples’ hardness $H$ and Young’s modulus $E$. A constant Poisson’s ratio of 0.3 was assumed for all tested samples, since the error of this parameter usually results in a very small or negligible variation in the sample’s Young’s modulus. Furthermore, the successful, valid measurements of the 100 indents were averaged to obtain their mean and standard deviation of each sample.

4.2.7 Unconfined Compression Testing

For each sublayer, one of the two ~10 × 10 × 10 mm cubes was used for the unconfined compression testing in an automated GeoJac loading frame (Trautwein Soil Testing Equipment, Inc., TX, USA) with a maximum load capacity of 8,918 N and a load resolution of 0.1 N. Prior to testing, a thin layer of silicone vacuum grease was applied to the top and bottom surfaces of the cube sample that were in contact with the loading platens to minimize the friction and hence the end effect. Load was monotonically increased at a constant strain rate of 0.5%/hr until the specimen failed by crushing.
4.3. RESULTS AND DISCUSSION

4.3.1 Superhydrophobicity

Figure 4.5 shows the superhydrophobic nature of both pure and graphene-reinforced T/Q siloxanes. The former has a WCA of $\sim 162.6^\circ$ (Figures 5a and 5d) and $165.4^\circ$ (Figures 4.5b and 5e) for the dry powder and solid block of Sample T25-0G respectively, indicating that the pure T/Q siloxane is superhydrophobic. As shown in Figures 4.5c and 5f, adding 0.9 wt.% graphene nanoplatelets into the T/Q siloxane slightly decreases the WCA to $156.6^\circ$, indicating that the composites are still superhydrophobic, despite that graphene is typically slightly hydrophilic with a WCA of $42^\circ$ (Prydatko et al., 2018). Moreover, simple visual examinations found that nearly spherical water droplets form on any fractured surface and on the ground dry powder (Figures 4.5d-5f), further suggesting that the synthesized siloxanes have three-dimensional (3D) voluminous superhydrophobicity.

![Figure 4.5 Water contact angles: (a) water contact angle for the smooth surface of powder SHOIP; (b) water contact angle for the smooth surface of solid SHOIP; (c) water contact angle for the smooth surface of solid MMG at 9 wt. ppt; (d) water contact angle for the natural surface of powder SHOIP; (e) water contact angle for the natural surface of solid SHOIP; (f) water contact angle for the natural surface of solid MMG at 9 wt. ppt.](image)
In general, a superhydrophobic surface with a WCA of >150° results from two important features: (1) the surface material or layer must possess a low surface energy, usually due to the presence of non-polar moieties (e.g., nonpolar functional groups such as -CH₃, -CF₃, -SiO₄); (2) the surface has hierarchical roughness, usually at multiple scales (e.g., from nano to micro and to millimeter) (Michael & Bhushan, 2007; C. Yang et al., 2006). In fact, the currently achievable maximum WCA of a smooth surface is ~119 to 120°, from a manufactured material with its surface covered by fluorocarbons (i.e., -CF₃). The above WCA data validate that the siloxane’s interior surface is covered by -SiCH₃ groups that lower the chemical energy and hierarchical roughness that further enhance the hydrophobicity. As discussed later, the nature of superhydrophobicity and hierarchical roughness can significantly lower the thresholds for cavitation nucleation and bubble information and growth due to heating (i.e., thermal cavitation) or ultrasonication (i.e., acoustic cavitation), which were employed during sample preparation to promote better dispersion and distribution of graphene.

4.3.2 Porosimetry

Figure 4.6 shows some selected MIP results for the purpose of comparison, while the total porosity and bulk density of all samples are compared in Table 4.1. The four samples (i.e., T25-U, T25+U, T50+U, and T75+U+W) exhibit the same shape of the cumulative intrusion volume versus pore diameter curves, where a critical pore size of ~700 to 1000 nm exists (Figure 4.6a). Most pore sizes are in the range of ~300 to 1000 nm, with a small percentage of smaller pores of ~30 to 300 nm (Figure 4.6b). Of the 4 samples, the T25-U (i.e., without ultrasonication dispersion) has the smallest pore sizes and total porosity, while the T75+U+W with 30 wt.% more water has the largest characteristics pore sizes and total porosity. Sample T50+U shows a section of combined peaks at the pore size of ~25-100 nm, which might be caused by certain micro/nano cracks. Moreover, the total porosity increases with curing temperature (Table 4.1). The special one, T75+U-W with 30 wt.% more water, of course possesses a reduced porosity due to the reduced water content. To conclude, the MIP results indicate that the total porosity of these samples increases with curing temperature, ultrasonication, and water content, while the bulk density exhibits the opposite trend. Since porosity or bulk density actually reflects the packing of the material and existence of defects (e.g., pores or cracks), both of these properties can be used to assess the mechanical properties of
composites. As discussed later, the aforementioned variations of porosity are actually caused by acoustic and thermal cavitation and bubble formation induced by ultrasonication and heating respectively.

Figure 4. 6 Pore size distribution from MIP for the top part: (a) cumulative intrusion with pore diameter; (b) differential intrusion with pore diameter.
4.3.3 General Nanoindentation Results

Figure 4.7 shows typical nanoindentation testing results selected for the top sections of the two samples that both were cured at 25°C and contained 0.9 wt.% graphene, without and with precuring ultrasound dispersion of graphene, respectively: T25-U and T25+U (Table 2). Although each sample was subject to 100 indent measurements, some indents failed due to improper contacts or excessive cracking, and hence the number of valid measurements is less than 100 (e.g., Figures 4.7a and 7b have 69 and 65 curves respectively). In Figure 4.7a, quite a few curves characterized by large pop-ins, large $h_{\text{max}}$ and relatively lower $F_{\text{max}}$ may be caused by excessive cracking or the collapse of relatively large pores within the loading-induced elastoplastic zone beneath the indenter tip (G. Zhang et al., 2009). For the measured Young’s modulus and hardness, these curves are highly scattered and generally show a decreasing trend with increasing indentation depth. The highly scattered nature of these curves reflects small-scale, local heterogeneity, which is normal and typical for multiphase materials such as rocks, concretes, bones, and other composites. The depth-dependent behavior actually manifests the indentation size effect (ISE, (Huang et al., 2010)), and further discussion of ISE is out of the focus of this paper.

An important feature common to these four plots (Figures 4.7c to 7f) is that these four sets of curves exhibit large scattering at shallow depths (e.g., $h < 2000$-3000 nm), but then become nearly constant at larger depths (e.g., $h > 4,000$ nm), especially for the Sample T25+U. Furthermore, the averaged line for each set of these curves is also plotted to a depth of 10,000 nm for comparison, which shows the same trend of variation with increasing indentation depth. As such, the average $E$ and $H$ values at $h = 8,000$ nm are considered as the mesoscale (e.g., ~100s μm) representative mechanical properties of each respective sample. Further discussion on the different behavior of these two samples will be presented later.
Figure 4. 7 Nanoindentation results for top parts: (a) Load with indentation depth for T25-U; (b) Load with indentation depth for T25+U; (c) Young’s modulus with indentation depth for T25-U; (d) Young’s modulus with indentation depth for T25+U; (e) Hardness with indentation depth for T25-U; (f) Hardness with indentation depth for T25+U.
4.3.3 Effect of Ultrasound Dispersion

Figure 4.7 can also be used to compare the scattering of the mechanical properties mitigated by ultrasound dispersion. The three sets of curves on the left plots (Figures 4.7a, 7c, and 7e) for Sample T25-U are clearly more scattered and have higher variations than the counterparts on the right for the T25+U. Here the $E$-$h$ curves are used as an example. For Sample T25-U (Figure 4.7c), although a few curves show really higher $E$, which may be caused by the aggregated graphene nanoplatelets due to van der Waals attraction, there are some really small $E$ curves too, most likely due to the lack of graphene reinforcements in the indented spots. In contrast, these $E$-$h$ curves from Sample T25+U (Figure 4.7d) are less scattered and fall into a narrow band. Further noteworthy is that these curves were obtained from a $10 \times 10$ matrix of indents, equivalent to an area of $2700 \times 2700$ nm. Such contrast validates that ultrasonication can really enhance the small-scale, localized homogeneity of the T/Q Al-siloxane composites. It is well known that ultrasonication treatment of colloidal dispersions, nanoparticle or nanomaterial (e.g., carbon nanotube, graphene) suspensions, and other sol-gel systems can effectively promote the uniform dispersion and distribution, and hence T25+U exhibits a higher stiffness and hardness than T25-U, in spite of some localized strengthening likely caused by the graphene aggregates (e.g., the larger $E$ values in Figure 4.7c).

At the mesoscale, Figure 4.8 shows the Young’s modulus and hardness values obtained by averaging all valid indentation measurements. Clearly, the three curves corresponding to the top, middle, and bottom sections of both samples, T25+U and T25-U are all scattered: in general, the top section has the highest $E$ and $H$, while the bottom section is the lowest, indicating that the mesoscale (i.e., centimeter scale) heterogeneity cannot be eliminated by ultrasonication, and hence some other factors may have contributed to it. A comparison of the densities of graphene and of some typical Al-silicates reveals that graphene is much lighter than the Al-siloxane, and hence graphene tends to move upward within the precursor slurry during curing, prior to the hardening of the precursor (Figure 4.4a). As such, although dispersion and distribute of the graphene nanoplatelets were achieved during sample syntheses, nonuniform distribution, particularly along the vertical direction, of graphene may result from the floatation of graphene. The completely cured sample may be stronger in the top section, while the bottom section may be weaker due to much less graphene reinforcement. This kind of heterogeneity was validated by the vertical
coloration of the completely cured samples: during trimming, it was observed that the top section has a much darker color than the bottom one, and some purely black dark spots were also observed on the top surface of the completely cured sample, clearly suggesting that, despite ultrasonication, graphene nanoplatelets can still aggregate and float upward. Moreover, such kind of heterogeneity cannot be revealed by macroscopic mechanical testing (e.g., unconfined compression), but by nanoindentation or other localized characterization techniques.

Moreover, and the scattered than the counterparts of the Sample T25-U (Figures 4.4c and 4d). Therefore, at 25°C curing temperature, Sample T25+U is more uniform at the meso (i.e., a few centimeter) scale. Overall, as summarized in Table 4.2 and Figure 4.12, pre-curing ultrasonication of the precursor slurry can effectively promote the dispersion of the graphene nanoplets and hence leading to the cured T/Q composites with better the microscale and mesoscale homogeneity of changed with indentation depth, and the sample cured with ultrasonic waves has higher Young’s modulus and hardness than the sample cured without ultrasonic waves, and the difference among the three layers is less than the other three layers cured without the ultrasonic waves. That indicates ultrasonic waves not only improve the strength of the composite but also help to disperse graphene better in the vertical direction.
Figure 4.8 Nanoindentation results for MMG at 9 wt. ppt: (a) Young’s modulus with indentation depth for T25+U; (b) Young’s modulus with indentation depth for T25-U; (c) Hardness with indentation depth for T25+U; (d) Hardness with indentation depth for T25-U.

4.3.4 Effect of Curing Temperature

Figure 4.9 presents the mechanical properties of the three samples, T25+U, T50+U, and T75+U, which were cured at 25, 50, and 75°C, respectively, but subject to same processing conditions (e.g., ultrasonication, water content). The T25+U exhibits the largest variation in mechanical properties along the specimen’s height, indicating nonuniform distribution of the added graphene nanoplatelets along the vertical direction (i.e., stronger top section with more graphene and weaker bottom section with less graphene due to floating). However, the three
sections from the T50+U and T75+U show similar, smallest variation in both Young’s modulus and hardness, suggesting that the property alteration along the height of these two samples become smaller or even diminish at elevated curing temperatures. Therefore, the higher-temperature curing can effectively lead to more uniform distribution of graphene along the vertical direction.

On the other hand, T50+U and T75+U both show smaller Young’s modulus and hardness than T25+U, but the latter has a more pronounced ISE at shallow depths (e.g., to depths of ~4000 nm, Figures 4.9a and b). When their total porosity and bulk density (Table 4.1) are compared, the reduction in mechanical properties caused by high-temperature curing is consistent with the increase in total porosity or decrease in bulk density, indicating that higher-temperature curing can increase the total porosity and hence reduce the bulk density, and the fundamental physical mechanisms (i.e., thermal cavitation on superhydrophobic surfaces) for such effects will be discussed later.

Furthermore, for a multiphase composite consisting of relatively coarse solid inclusions embedded within a relatively homogeneous fine-grained matrix (e.g., shale, concrete, OPC-treated clays), the observed ISE or the variation of Young’s modulus with depth at shallow depths also reflects the small-scale, localized heterogeneity of mechanically-distinct phases with the bulk composite (Y. Li et al., 2022; Luo et al., 2020). According to Figure 4.9, T25+U shows the ISE up to a depth of ~4000 nm, while the ISE of the other two samples, T50+U and T75+U, ends at a depth of <1500 nm. The studied bulk composites should consist of pure siloxane matrix, dispersed graphene, graphene aggregates of different sizes, and pores. As such, due to the slow hardening/curing rate of T25+U at a lower temperature, despite the ultrasonication pretreatment to disperse graphene during sample processing, the relatively longer hardening time at 25°C can allow the self re-aggregation of the previously dispersed graphene, thusly making the sample more heterogeneous via graphene aggregates, which exhibit higher elastic modulus and hardness as detected by nanoindentation. In contrast, the quick hardening of T50+U and T75+U leaves little time for the self re-aggregation of the previously dispersed graphene, and hence these two samples are more uniform in terms of mechanically distinct phases (e.g., pure siloxane matrix, dispersed graphene, much smaller graphene aggregates), thusly exhibiting less pronounced ISE that ends at much shallow depths. In fact, T75+U exhibits the smallest ISE with indentation depth.
Figure 4. 9 Nanoindentation results for MMG at 9 wt. ppt at different temperatures: (a) Young’s modulus with indentation depth for T25+U; (b) Hardness with indentation depth for T25+U; (c) Young’s modulus with indentation depth for T50+U; (d) Hardness with indentation depth for T50+U; (e) Young’s modulus with indentation depth for T75+U; (f) Hardness with indentation depth for T75+U.
4.3.5 Effect of Precursor Viscosity

Figure 4.10 compares the mechanical properties of the three samples, T75+U, T75+U-W, T75+U+W, which were prepared at different water to solid ratios and hence different viscosities of the precursor slurry (i.e., by decreasing or increasing the amount of water by 30 wt.% used for sample preparation) but were subject to the same curing temperature (i.e., 75°C) and ultrasonication. Clearly, the variation of properties of the three sections (i.e., top, middle, and bottom) within each sample is relatively small, especially at large depths (e.g., >4000 nm), suggesting that at the curing temperature of 75°C the distribution of the graphene within each sample is relatively uniform. This is true even for the one prepared with 30 wt.% less water, T75+U-W. However, at shallow depths, the properties vary considerably for T75+U+W and T75+U-W. The underlying reason may be different for these two samples. For T75+U+W (Figures 4.9c and 9d), the precursor sol has a much lower viscosity (or smaller viscous drag force) due to extra 30 wt.% more water, and hence the previously ultrasound-dispersed graphene can easily re-aggregate, which introduces larger local heterogeneity. A secondary reason for this shallow-depth heterogeneity is probably the relatively larger pores due to increased water content. On the contrary, for T75+U-W (i.e., with 30 wt.% less water), the precursor sol has a much higher viscosity, which increases the damping of the ultrasonic waves and hence makes the ultrasonication dispersion ineffective. As such, the graphene may experience little dispersion and still remain as the original aggregates, resulting in larger local heterogeneity.

In terms of the averaged mechanical properties, the T75+U-W (i.e., 30 wt.% less water) has the highest $E$ and $H$, while the opposite is true for T75+U+W (i.e., 30 wt.% more water). As discussed later, a higher temperature (e.g., 75°C) usually promotes the reaction kinetics (e.g., hardening or setting rate) and hence the precursor sol hardens and sets more quickly, which leaves little time for the graphene to move upward via floatation or buoyancy. Therefore, all these three samples are relatively uniform macroscopically along the sample height, since the graphene does not have time to move up freely in the precursor slurry, even for the sample with a much-reduced viscosity due to 30 wt.% more water, because of the fast setting and hardening of the siloxane matrix. However, the localized shorter-distance re-aggregation at the microscale can still take place, which introduces graphene aggregates into the composites, resulting in a more pronounced ISE.
For all studied samples, Figure 4.11 compares their Young’s modulus and hardness extracted at the depth of 8000 nm together with the error bars representing ±1.0 standard deviation. The T25-U (i.e., no ultrasonication) has the largest errors, suggesting again that this composite, especially the top section, has the largest heterogeneity (due to non-dispersed graphene aggregates as well as graphene floatation). The top section of this sample also has the highest $E$ and $H$ among all these samples, further validating that this section possesses the highest fraction of graphene, due to flotation of graphene aggregates. With increasing curing temperature, the composites become weaker, and the difference in the mechanical properties of the samples cured at 50 and 75°C is very small. Of course, T75+U-W exhibits a small increase in the mechanical properties due to reduced water content and hence smaller total porosity (Table 4.1).
Figure 4. 10 Nanoindentation results for MMG at 9 wt. ppt at different viscosities: (a) Young’s modulus with indentation depth for T75+U; (b) Hardness with indentation depth for T75+U; (c) Young’s modulus with indentation depth for T75+U+W; (d) Hardness with indentation depth for T75+U+W; (e) Young’s modulus with indentation depth for T75+U-W; (f) Hardness with indentation depth for T75+U-W.
Figure 4. Nanoindentation results for three layers under different curing conditions: (a) Young’s modulus with error bars at the depth of 8 µm; (b) Hardness with error bars at the depth of 8 µm.
4.3.6 Unconfined Compression Testing

Figure 4.12 shows the stress-strain curves of all unconfined or uniaxial compression tests performed on the small cubic samples cured under different conditions, while the corresponding failure strength data are compared in Figure 4.13. Overall, Sample T25+U (i.e., subject to ultrasonication and 25°C curing) exhibits the highest strength and stiffest slopes (i.e., Young’s moduli), while Samples T75+U and T75+U+W (i.e., ultrasonication, 75°C curing, and without and with 30 wt.% more water respectively) has the lowest strengths and Young’s moduli. To summarize, the average Young’s moduli (Table 4.2) and failure strength (Figure 4.13) of all samples in general decrease with curing temperature and water content, clearly reflecting that high-temperature curing leads to a less stiffer material, which is contrary to the published general findings obtained for other cementitious materials such as ordinary Portland cement and geopolymers, which are both hydrophilic. Such abnormal behavior warrants further discussion in a later section.

Table 4. 2 Young’s modulus of each sample for the unconfined compression test.

<table>
<thead>
<tr>
<th>Test Position</th>
<th>T25+U</th>
<th>T25-U</th>
<th>T50+U</th>
<th>T75+U</th>
<th>T75+U+W</th>
<th>T75+U-W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>5.8</td>
<td>8.3</td>
<td>3.6</td>
<td>3.0</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Middle</td>
<td>7.3</td>
<td>6.3</td>
<td>3.5</td>
<td>2.5</td>
<td>2.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Bottom</td>
<td>6.8</td>
<td>5.6</td>
<td>4.0</td>
<td>2.9</td>
<td>2.6</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Regarding the variability among the different sections of a given sample (i.e., since the small cubes were cut from the top, middle, and bottom sections of a larger cylindrical sample), clearly, the 3 curves for Sample T75+U and T75+U+W are the least scattered, while those for the T25+U and T25-U are highly scattered, indicating that high-temperature curing can result in a more uniform material with similar mechanical properties along the height. This observation is consistent with the results of nanoindentation testing: curing at higher temperatures can lead to more uniform samples. In other words, although 25°C curing and ultrasonication can increase the strength of the composite, but this temperature is not ideal to achieve a homogeneous composite, as reflected by the local variability of strength within the same cylindrical sample. Finally, the amount of water has very minor influence on the local variability, although it can affect the strength.
considerably. Reduced water content can increase the strength but may also make uniform dispersion of graphene more difficult, simply due to the increased viscosity that makes ultrasonication less effective.

In conclusion, these macroscopic testing results are consistent with the counterparts of nanoindentation testing. That is, ultrasonication of the initial precursor sol only promotes the local small-scale dispersion and hence helps improve the strength of the composite. Higher temperature curing at 50 and 75°C can achieve a macroscale more homogenous composite (i.e., along the height), but may cause opposite effects on the strength and stiffness.
Figure 4. 12 Unconfined compression results for MMG at 9 wt. ppt at different curing conditions: (a) unconfined compression for T25+U; (b) unconfined compression for T25-U; (c) unconfined compression for T50+U; (d) unconfined compression for T75+U+W; (e) unconfined compression for T75+U; (f) unconfined compression for T75+U-W.
4.4. DISCUSSION

4.4.1 Small-scale Homogeneity and Graphene Dispersion

It is well known that those nanomaterials, including nanofibers, nanoparticles, and nanosheets, tend to aggregate in suspension due to relatively significant surface forces (e.g., van der Waals attraction), and hence making a stable dispersion of nanomaterials is difficult. Such aggregation phenomena have been observed in clay-polymer nanocomposites (Hajibeygi et al., 2015; Zare, 2016) and carbon nanotube-cement composites (Wansom et al., 2006). In this study, improved dispersion of graphene nanoplatelets within the precursor slurry was achieved by ultrasonication, and the nanoindentation results from Samples T25+U and T25-U clearly demonstrate that ultrasonication can result in better small-scale homogeneity by breaking down the graphene aggregates, and hence a higher strength can also be obtained from the ultrasound-treated composites. Moreover, since graphene is slightly hydrophilic and the cured siloxane with
-SiCH₃ on its exterior surface is superhydrophobic, graphene is not highly miscible or dispersible within the hydrophobic siloxane precursor. Therefore, for all other samples, ultrasonication was applied to sample preparation and processing to achieve a more uniform small-scale dispersion of graphene nanoplatelets and hence the small-scale homogeneity of the composite. In general, a more uniform material with no weak links or defects should behave stronger than the nonuniform counterpart with the weakest links.

Since the ultrasonication-induced disintegration of graphene aggregates is reversible, the previously dispersed graphene nanoplatelets can re-aggregate again, at least for the local scale, if they are not frozen or prevented from movements (e.g., flotation, lateral transition). As such, if the hardening rate is not fast enough to instantaneously fix the graphene nanoplatelets in place, they can form smaller aggregates, but may not float upward too much. In this case, the cured composite may exhibit relatively macroscale homogeneity but microscale heterogeneity, and the relatively minor ISE observed on some composites cured at elevated temperatures (e.g., 50 and 75°C) is actually the mechanical manifestation of such a microscale heterogeneity caused by graphene re-aggregation (Figure 4.14).

### 4.4.2 Large-scale Heterogeneity and Graphene Distribution

The large-scale distribution refers to the variation of graphene content along a sample’s height or vertical direction. Since graphene consisting of only carbon arranged in a nano-layered structure has a much smaller density than the Al-siloxane precursor, graphene, either dispersed or aggregated, tends to float upward due to buoyancy. As a result, although significant effort such as mixing and ultrasonication was made to achieve graphene’s uniform dispersion and distribution, the nanoplatelets, once the precursor slurry was casted into the curing molds, can transport under flotation along the vertical direction, and such movement does not stop until the precursor slurry hardens or reaches a certain stiff consistency, so as to freeze the graphene in place and stop its movement. This process induces large-scale heterogeneity and nonuniform distribution along the sample’s height: there are more graphene nanoplatelets in the top section of the sample than the bottom one. As a result, the top section of the sample exhibits higher strength and stiffness than the bottom one.
According to reaction kinetics, a higher temperature usually accelerates the reaction rates and hence faster curing of the siloxane precursor can be achieved. In other words, graphene’s upward floatation and the precursor’s hardening are two competing processes during curing: while graphene tends to move upward in a soft slurry, the hardening process tends to prevent such movement by freezing it. Therefore, higher-temperature curing, which accelerates the hardening of the precursor slurry, can mitigate or prevent the graphene’s upward movement, and hence the meso or macro scale uniform distribution of graphene along the vertical direction can be achieved. This logically leads to samples with macroscale uniform mechanical properties (e.g., for Sample T75+U+W).

4.4.3 Negative effects of Acoustic and Thermal Cavitations

The above interpretation and discussion still fail to uncover the mechanisms for the reduced strength and stiffness caused by high temperature curing and ultrasonication, since most cementitious materials cured at higher temperatures exhibit better mechanical performance (Choi et al., 2022; Q. Liu et al., 2016). In this study, such detrimental effects of ultrasonication and/or heating are actually the manifestation of superhydrophobicity of the siloxane. In general, superhydrophobicity is characterized by two important features: a low intrinsic surface energy and hierarchical surface roughness. As discussed early, the siloxane has a WCA of > 162-165° (Figure 4.5) and hence is superhydrophobic. Besides the -SiCH\textsubscript{3} on the exterior (Figure 4.14e) and interior surfaces (since the siloxane is 3D superhydrophobic), surface roughness must also be present (Figure 4.14a to 14c). As such, small air bubbles may be entrapped within the small cavities on the rough or hydrophobic surfaces (Figure 4.14a to 14c) due to hydrophobic attraction (Krasowska et al., 2009), which may be introduced to the precursor slurry through mixing or simply adsorption on the graphene surface. Both acoustic and thermal cavitations have a much lower threshold for bubble nucleation and formation on superhydrophobic surfaces (Jin et al., 2016b, 2017). As such, higher-temperature curing can result in the formation of bubbles and cavitations, some of which may not grow to the critical sizes large enough to implode, and hence remain as vapor or air cavities in the completely cured siloxane, resulting in an increased total porosity. In fact, the direct porosity and density measurements prove this mechanism (Table 4.1). A material with higher porosity and lower density in general has lower strength and stiffness. Such a detrimental effect caused by
thermal or acoustic cavitations may not be pronounced or observed in hydrophilic cementitious materials (e.g., Portland cements, geopolymers), and hence cement and concrete cured at elevated temperatures usually exhibit improved strength and stiffness. Results and findings from this study actually contradict the widely recognized knowledge on high-temperature curing. Therefore, extra caution should be taken in applying material processing and curing techniques developed for hydrophilic materials to the hydrophobic or superhydrophobic counterparts.

Finally, despite these negative effects, the siloxane-graphene nanocomposite still achieves a macroscale compressive strength of up to ~34 MPa, well exceeding the counterparts of some OPCs (e.g., Type I and II have an unconfined compressive strength of 19 and 17 MPa, respectively, (Designation: C150/C150M – 22 Standard Specification for Portland Cement 1, n.d.)). Yet, the composite is still superhydrophobic and hence may furnish other functionalities such as self-cleaning, anti-fouling, viscous drag reduction, and water harvesting. Moreover, graphene is also highly thermal and electrically conductive, which can also render the composite additional functionalities such as thermal and electrical conductivity. As such, this study can shed light on the future development of superstrong, thermally and electrically conductive, voluminously or 3D superhydrophobic, and porous nanocomposites, which may find viable applications such as water-repellency, highly durable cementitious materials, sensing materials, and drag-reduction surface coatings, among others.
4.5 CONCLUSIONS

This paper presents an experimental study of the effects of ultrasonication, heating, and precursor viscosity on the microscale dispersion and macroscale distribution of reinforcing graphene in a superhydrophobic T/Q siloxane. According to the above analysis and discussion, the following conclusions can be drawn:

- Microscale dispersion and hence uniformity of the graphene-siloxane nanocomposites can be achieved by ultrasonication. However, slow hardening may void the ultrasonication
treatment, since graphene nanoplatelets can re-aggregate if they are not fixed instantaneously or immediately after ultrasonication.

- A usually missing phenomenon for adding graphene to sol-gel-based material synthesis is its tendency for upward flotation, which can cause nonuniform distribution of the graphene.
- For the superhydrophobic siloxane, high-temperature curing tends to decrease the strength and stiffness of the nanocomposites and hence can be detrimental, due to the much lower thresholds for thermal cavitation on superhydrophobic surfaces.
- Nanoindentation testing can successfully detect the microscale heterogeneity caused by the aggregation of graphene nanoplatelets, while conventional unconfined compression testing on small cubes can discern the macroscale nonuniform distribution of graphene along the vertical direction.
- Graphene can be effectively used to reinforce superhydrophobic siloxane, and the resulting nanocomposite can achieve an unconfined compression strength of up to ~34 MPa.
- Extra caution should be taken in applying materials processing and treatment techniques developed for hydrophilic materials to superhydrophobic counterparts.
5. ISOThERMAL ADSORPTION FOR HYDROPHILIC AND HYDROPHOBIC MATERIALS

This paper presents the synthesized materials with alkali activation of metakaolin and hydrolysis of alkoxy silanes and uses isothermal adsorption to analyze the difference between these materials which include hydrophilic, superhydrophilic, hydrophobic, and superhydrophobic materials. To better study the influence of impact factors on the water adsorption for the four different materials, there are nitrogen adsorption to learn the surface area, the pore size of materials, water vapor adsorption to obtain the thickness of the water film, ultra-small-angle X-ray scattering and scanning electron microscopy to study the surface morphology. Based on the shape of curves, it is easy to tell the difference between hydrophilic and hydrophobic materials. The curves of materials that are affinity to water show Type II isotherms, but the curves of materials that are water-repellent present Type V. In addition, it is not a good way to tell hydrophilic and hydrophobic materials based on the capacity of adsorbed water, it should be combined with the thickness of the water film, the rate of adsorption under different pressures, surface morphology, pore size, and specific surface area.
5.1. INTRODUCTION

The water vapor adsorbed on solid surfaces has been widely studied in different fields from biology to material science. The layer of the adsorbed water film usually ranges from one to multilayer. Therefore, the film structure and adsorbed mechanisms are strongly influenced by the substrate (Gutian Zhao et al.). Between the adsorbate and the substrate, there are two types of adsorptions according to the interaction strength, which include chemisorption and physisorption. Physisorption happens because of the weak electrostatic interactions containing van der Waals interactions, dipole-dipole, and London forces, which are easily broken due to the weak bands (K. S. W. Sing, 1998). But chemisorption occurs when covalent bond forms between the adsorbate and the substrate with sharing or transferring of electrons (Qu et al., 2018). Thus, the interactions of chemisorption are much larger than that of physisorption. In chemisorption, the enthalpy is very high, and it happens at all temperatures, and it is irreversible (X. Guo & Wang, 2019). Physisorption has low enthalpy, but it just occurs at a low temperature below the adsorbate boiling point, and it is reversible (Mohammad et al.). A monolayer of adsorbate can be formed in chemisorption, and then the physisorption will take place with the multilayer formation of adsorbate on the substrate (M. C. Lu et al., 2016).

In geotechnical engineering, it is often to use water retention curves with controlled suction to study the fluid flow for unsaturated soils (N. Lu et al., 2014; Tang & Cui, 2011). There are three widely used controlled suction methods (Delage et al., 1998; Marinho et al., 2009; Ng et al., 2015): the axis translation technique applies porous ceramic stones for air and water pressure to flow, and the suction can be up to 14 MPa (Marinho et al., 2009); the osmotic technique utilizes polyethylene glycol solutions to make the suction can be up to 12 MPa; and the last one is vapor equilibrium technique, which has a large suction range (3-1000 MPa) (Blatz et al., 2009). Vapor equilibrium techniques (VETs) are often used to study swelling clays. The main advantage of VET over other relative humidity sensors is the capacity to obtain the target suction of soils. Besides, the adsorption and desorption behaviors can be explored effectively via VET. There are two types of VETs that are applied to produce constant suction conditions, which include and unsaturated acid solutions saturated salt solutions (Karagoly, 2020). The method of using the unsaturated acid solutions is hard to achieve the target suction value because the osmotic solution changes with the water exchange (Alonso et al., 2005). The second method is to choose the specific type of saturated salt
solution to achieve a certain relative humidity. The advantage of the saturated salt solutions is the concentration of the osmotic solution keeps the same as water exchange happened between specimens and the vapor environment (Erhardt & Mecklenburg, 2013; Winston & Bates, 1960).

It’s widely used to control high suctions for unsaturated soil tests with saturated salt solutions. The chemical solutions determine the water content in the closed container and that in the soil sample to reach equilibrium. Different saturated salt solutions show different values of relative humidity and corresponding suction (Greenspan, 1977). The VET was applied to control the suction of the specimen to determine the properties of unsaturated soils, but the large temperature fluctuation could influence the excessive condensation of water vapor leading to an excessive increase in water content in soils (Agus and Schanze, 2005). The property of water retention for unsaturated soils is related to various physical parameters and properties of the soil samples with the technique to control the suction (Pierre Delage, 2002).

Except for the VET, there is liquid-phase adsorption, such as nitrogen adsorption at 77K for quality control and the investigation of new materials. The first recorded studies about the adsorption of nitrogen were made by Dewar and Ramsay (James Dewar, 1905; Sir illiam R sa, 1905) when they investigated and separated the noble gases. Then lots of research about the adsorption of nitrogen at the liquid phase gradually came out. The Langmuir theory for monolayer adsorption and the Brunauer-Emmett-Teller (BET) theory offers theoretical support to interpret the data. The BET theory is often widely used to obtain the specific surface area (SSA) of materials and analyze the data to achieve the pore size of materials. The pore size and SSA are vital to study water vapor adsorption for different materials, especially for hydrophilic and hydrophobic materials.

Water vapor adsorption is different with other nonpolar gases, such as N₂, and CH₄, on hydrophilic and hydrophobic solid surfaces, it is more complicated and the adsorbed water molecules are tended to form the hydrogen bonds with the functional groups on the solid surfaces. Hydrophilic and superhydrophilic materials are affinity to water. The hydrophobic property of the surface reflects the materials’ chemistry and can be related to the interaction with water molecules. The hydrophobic or superhydrophobic material is water-repellent. Therefore, it is easy to conclude that hydrophilic or superhydrophilic materials could adsorb more water than hydrophobic or superhydrophobic materials under the same condition. However, the studies about telling the
difference of hydrophilic and hydrophobic are rarely reported, so it is expected that water adsorption isotherms can be highly informative in this paper.

Isothermal adsorption on solid surfaces, normally includes monolayer adsorption, multilayer adsorption, and capillary condensation. Adsorbed water on solid surfaces has been indicated to result in many adsorbed water monolayers, leading to conclude that isothermal adsorption needs to be precluded by the formation of an original adsorbed water layer on the external clay surfaces. There are lots of models to fit the experimental data, such as Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Toth, and other models. For monolayer adsorption, Langmuir equation, L-F (Langmuir-Freundlich) equation, and M-L (modified Langmuir) equation are normally used to estimate the adsorption and are valid at low pressure (Al-Ghouti & Da’ana, 2020a). The Langmuir model fits the adsorption on the homogeneous surface, but Gaussian energy distribution is usually used to adjust the heterogeneous system for monolayer adsorption. In terms of multilayer adsorption, Halsey isotherm model, the BET adsorption model, and Frenkel-Halsey (FHH) models are very popular. For the BET equation, it assumes the interaction on the adsorbent surface is much larger than that between neighboring adsorbate molecules, and it is suitable for adsorption on solid surfaces with homogeneous chemical properties (Foo & Hameed, 2010; Ladavos et al., 2012). The BET adsorption model is normally used to fit experimental water adsorption isotherms on clay minerals. The BET model is suitable for adsorption on the external surface at low relative humidity (RH) values, but it could not be used to represent adsorption on non-homogeneous surfaces at high RH values. Therefore, for the heterogeneous surfaces at high RH, it is necessary to figure out other models to fit. In the aspect of capillary condensation, it is widely to use the hybrid isotherm model, such as combining the Langmuir and the Sips equations with a set of parameters, which can represent well the adsorption data over a wide range of RH (Jae Lee et al.). The van Genuchten model is widely used to describe the Soil-Water-Characteristic Curve (SWCC) of a variety of soils, and it successfully fits the water retention curve at medium and high values of the water content. Therefore, some scholars used the extended van Genuchten model to describe capillary condensation at high pressure (Revil et al.).
5.2. MATERIALS AND METHODS

5.2.1. Materials

The as-received dry powder of PowerPozz™ metakaolin (MK, SiO₂·Al₂O₃) (Advanced Cement Technologies, LLC., WA, USA) was used as the raw material for alkali activation, and its particle size distribution measured by the relevant ASTM standard method and chemical compositions are shown in Table 3.1. The alkaline activator consisted of a mixture of sodium silicate solution (Na₂O·SiO₂·5H₂O, Ricca Chemical Co., TX, USA) and sodium hydroxide (NaOH, Fisher Scientific, Inc., USA). The former was a technical-grade solution with a 40°-42° Baume (i.e., an average density of 1.4 g/cm³ or specific gravity of 1.38 to 1.42 at 25°C) and pH 11.2, and consisted of 9.1, 29.2, and 61.7 wt.% Na₂O, SiO₂, and H₂O, respectively (Table 1), while the latter was white solid pellets with a >98% purity quotient. A trifunctional alkoxysilane (T-silane), nitrogen-flushed methyltrimethoxysilane (MTMS, CH₃Si(OCH₃)₃, 97%, Acros Organics, Inc., NJ, USA), was selected as the hydrolyzable agent to lower the surface energy via introducing the -SiCH₃ moieties to the siloxanes. Nitrogen-flushed 3-aminopropyltrimethoxysilane (APTMS, C₉H₂₃NO₃Si, 95%, Fisher Scientific, Inc., USA) was chosen to work as a hydrolyzable agent and offer the functional group (-NH₂) to the siloxanes. 2-cyanoethyltriethoxysilane (C₉H₁₉NO₃Si, >98%, Tokyo Chemical Industry Co., LTD) was selected as a hydrolyzable agent to provide the functional group (-CN) for the siloxanes. 10 types of salts were used to achieve certain relative humidity, which include: copper sulfate (CuSO₄) was achieved from Lab Chem, PA, USA; lithium bromide (LiBr) was offered by Tokyo Chemical Industry Co., LTD; potassium carbonate (K₂CO₃, 99+%) was provided by Acros Organics, NJ, USA; zinc sulfate (ZnSO₄), magnesium nitrate (Mg(NO₃)₂, ammonium nitrate (NH₄NO₃), magnesium chloride (MgCl₂), lithium chloride (LiCl), potassium chloride (KCl), and sodium chloride (NaCl) were purchased from Fisher Scientific, Inc., USA,
5.2.2. Synthesize Procedures

The general process for the synthesis of the T/Q siloxane consisted of alkali activation of the amorphous aluminosilicate (i.e., metakaolin), hydrolysis of the T silane MTMS or APTMS, and hybrid co-condensation of alkali-activated inorganic silanols and Na-aluminols as well as hydrolysis generated organic methyl silanols. The pure T/Q siloxane was pre-designed to have a fixed nominal Si/Al, Na/Al, and T/Q molar ratio of 1.7, 1.0, and 0.0625, respectively, and the silicon in the Si/Al ratio included the Si from both the trifunctional (T, RSiO$_{3/2}$, where R is an organic radical) and tetrafunctional (Q, SiO$_{4/2}$) structural units. Such a T/Q siloxane was superhydrophobic due to the grafting of methyl (i.e., -CH$_3$) groups into the siloxane at its end or surface, and superhydrophilic because of the functional groups (i.e., -CN).

The synthesizing method is a facile, green, sol-gel-based activation-hydrolysis-condensation technique, which integrates alkaline activation of amorphous aluminosilicates and hydrolysis of organosilanes with hybrid condensation. The synthesis process began with preparing the alkali activator solution (Figure 5.1) via dissolving NaOH pellets in de-ionized water, followed by adding a certain amount of sodium silicate solution. Upon complete cooling of the mixture to room temperature, MK powder was added to the activator solution, followed by continuous mixing for 20-30 min to achieve complete dissolution, leading to a viscous slurry containing activated silanols and Na-aluminols. Then the desired amount of material with functional groups, such as MTMS, or APTMS was added dropwise with a pipet to the slurry while it was still being continuously stirred to accelerate the uniform distribution of the material with functional groups. This step usually took 20-30 min to complete and was followed by at least 15 min continuous mixing to promote the breakdown and hydrolysis of initially immiscible organosilanes droplets.

The final homogenized slurry was then cast into half-split cylindrical high-density polyethylene molds with an inner diameter and height of 2.54 and 6.35 cm respectively. Which has been coated with a thin layer of vacuum grease on the inner surface, to facilitate subsequent demolding (Figure 5.2). The slurry samples in the molds were initially cured at room temperature for 7 days, followed by demolding and further curing in the air for at least 7 days until they were dried completely, as indicated by no further change in their mass.
Figure 5.1 Synthesize procedures
Figure 5. 2 Molds for curing samples: (a) a completely disassembled mold showing the two split half cylinders and two end caps; (b) a fully assembled mold with a cured sample; (c) superhydrophobic materials with water droplets; (d) superhydrophilic materials with water droplets penetrated through it (as shown in red dash circle).

5.2.3. Sample Preparation

To investigate the behaviors of adsorption and desorption for hydrophilic and hydrophobic materials, the completely cured and dried cylindrical samples needed to be finely ground as powder. The powder was obtained by hand-grinding a piece of fractured sample in a mortar and pestle to pass all materials through a #325 mesh (i.e., an opening size of 44 μm). All powders need to be completely dried in a clean oven for 24 hours before putting into the sealed container.
5.2.4. Adsorption Isotherm

In this paper, the water vapor adsorption experiment was determined to do the adsorption isotherms. Water vapor adsorption is an important method to learn the subtle changes in micro and pore structure because water evaporation can be tested at various length scales. Water vapor sorption measurements were performed with the method of VET because all soil specimens are treated as clays. As shown in Figure 5.3, environments of constant humidity can be made with sealed containers using saturated salt solutions at the bottom. The glass desiccator with a porous plate over the saturated solution, so the soil specimens can be put on the porous plate to absorb the water vapor in the constant relative humidity. The partial vapor pressure produced by the environment in the desiccator is directly related to the concentration of the solution. Adsorptions are created in soil specimens with the water interchange between the specimen and the vapor in the top space of the desiccator. In this study, there are 10 types of salt were chosen to achieve different relative humidity. Also, there are 10 sealed containers to make the constant relative humidity based on 10 types of saturated salt solutions, the edges of the container need to be coated with a thin layer of silicone vacuum grease to prevent air to seal the containers. Hence, the range of the relative humidity is 6% to 97% (Table 5.1).

![Figure 5.3 Soil specimens in the constant relative humidity of a sealed container (Blatz et al., 2008).](image)

In this paper, the temperature for adsorption and desorption is 25°C ± 1°C. For the adsorption of water vapor, the time taken by soil specimens to get the equilibrium is about 1 month. Then put all specimens in the desiccator with pure water to maintain the relative humidity is 100%,
after achieving the equilibrium (on change of the weight of samples), then put them back in the desiccators with saturated salt solutions to complete the desorption. Finally, the desorption to achieve equilibrium is about 2 weeks.

Table 5.1 Types of salt and the relative humidity

<table>
<thead>
<tr>
<th>Saturated salt solutions</th>
<th>CuSO₄</th>
<th>ZnSO₄</th>
<th>KCl</th>
<th>NaCl</th>
<th>NH₄NO₃</th>
<th>Mg(NO₃)₂</th>
<th>K₂CO₃</th>
<th>MgCl₂</th>
<th>LiCl</th>
<th>LiBr</th>
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<tr>
<td>(Copper Sulfate)</td>
<td>97</td>
<td>90</td>
<td>84</td>
<td>75</td>
<td>65</td>
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<td>43</td>
<td>33</td>
<td>11</td>
<td>6</td>
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<tr>
<td>(Zinc Sulfate)</td>
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<td>(Potassium Chloride)</td>
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<td>(Ammonium Nitrate)</td>
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<td>(Lithium Bromide)</td>
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</tbody>
</table>

Relative humidity (%)

| 97 | 90 | 84 | 75 | 65 | 55 | 43 | 33 | 11 | 6 |

The synthesized materials are not pure because there are some remained materials after alkali reactions, hydrolysis, and co-condensation. To investigate whether the remained materials will influence the adsorption capacity, two groups of each sample are designated as “C” and “U” hereafter, respectively (Table 5.2). Unclean means these materials were synthesized with the above procedures, and the surfaces are not pure because the surfaces have lots of other remained materials after chemical reactions, like sodium hydroxide, sodium bicarbonate, and sodium carbonate. However, for U-MK, it does mean the surface was not washed with ethanol and water, it was used directly after purchasing from the company. The clean materials mean the surfaces were washed with ethanol and water several times and dried the powders completely, so the clean materials are completely pure materials without any remained materials on the surfaces.

Table 5.2 Samples for isotherm adsorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydrophobic material</th>
<th>Superhydrophobic material</th>
<th>Hydrophilic material</th>
<th>Superhydrophilic material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unclean</td>
<td>U-AO</td>
<td>U-SHOIP</td>
<td>U-MK</td>
<td>U-Cyano</td>
</tr>
<tr>
<td>Clean</td>
<td>C-AO</td>
<td>C-SHOIP</td>
<td>C-MK</td>
<td>C-Cyano</td>
</tr>
</tbody>
</table>
5.2.5. Nitrogen Adsorption and Specific Surface Area

Nitrogen adsorption (NA) experiments were conducted at liquid nitrogen temperature (77.3 K) with an ASAP 2460 volumetric adsorption analyzer under high-vacuum conditions (Micrometritics Instrument Corp., Norcross, GA). Powder samples of roughly 0.5g for each material were used on average in each adsorption experiment. All samples were needed to outgas at 120°C overnight prior to the adsorption measurements.

According to the NA experiment, Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area (SSA) and porosity of all powdered materials. It is assumed that nitrogen can access the entire surface of the materials, and the occupation probability of a site is not related to the occupancy of neighboring sites (Jaroniec et al., 1999; Włodarczyk-Stasiak & Jamroz, 2009). The SSAs were measured with the adsorption of gas molecules in infinite layers without interlayer interaction. Based on the above, the Langmuir theory can be used for every layer to obtain the BET surface area of each material (Table 5.3).

\[
S = \frac{V_0 N_a s}{M_V \alpha}
\]  

(5.1)

where \(S\) is the specific surface area, the \(V_0\) is the volume of each monolayer of adsorbed gas, \(N_a\) is Avogadro’s number, \(M_V\) is the molar volume of gas adsorbed, \(\alpha\) is the mass of the solid sample, and \(s\) is the surface area of a single gas molecule adsorbed on the solid.

<table>
<thead>
<tr>
<th>Material</th>
<th>C-AO</th>
<th>C-SHOIP</th>
<th>C-MK</th>
<th>C-Cyano</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA (m²/g)</td>
<td>44.99</td>
<td>27.83</td>
<td>13.91</td>
<td>24.13</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>7.21</td>
<td>15.36</td>
<td>N/A</td>
<td>12.09</td>
</tr>
</tbody>
</table>

According to the specific surface area \(S\) achieved from Equation (5.1) and the known quantity of adsorbed water on the external surfaces of samples, it is easy to calculate the thickness of the water layer adsorbed on the surface based on Equation (5.2) (Dolinar & Macuh, 2016). The
isotherm thickness is related to relative humidity, surface chemistry, and surface roughness of the solids.

\[ w = S \cdot h \cdot \rho \]  \hspace{1cm} (5.2)

where \( w \) is the water content, \( h \) is the thickness of water, and \( \rho \) is the density of water.

Pore size distribution was calculated by BJH (Barret-Joyner-Halenda) method, which is appropriate for mesoporous materials, and the range is about 2nm \( \sim \)50nm (K. Sing, 2001). It uses the modified Kelvin equation to calculate the amount of adsorbate removed from the pores of the material with the relative pressure decreasing from a high to a low value to the size of the pores. There are two basic assumptions for this method: 1) the shape of the pore is cylindrical, and 2) the adsorbed amount comes from both physical adsorption on the pore walls and capillary condensation in mesopores.

Therefore, the isotherm thickness, thermodynamics, particle size and SSA of samples, and hydrogen-bonding interactions of water molecules adsorbed on hydrophilic and hydrophobic surfaces are studied and compared in this paper.

5.2.6. Ultra-Small-Angle X-ray Scattering (USAXS)

USAXS is a nondestructive measurement test in which the elastic scattering of X-rays from heterogeneous within a sample is recorded at low scattering angles. USAXS data include information about parameters, like the size, shape, volume, and total surface area of the scatters, as well as the characteristic distances between those scatters that are ordered or partially ordered. All data in this paper were achieved from the USAXS instrument at the Advanced Photo Source (APS) at Argonne National Laboratory (Lemont, IL, USA). The instrument has angular and energy resolutions of the order of \( 10^{-4} \), accurate and repeatable X-ray energy tunability over its operational energy range from 8 to 18 keV, and a dynamic intensity range of \( 10^8 \) to \( 10^9 \), according to the configuration. The scattering vector range is between 0.0001 to 1 \( \text{Å}^{-1} \).

USAXS is an excellent tool to quantitatively characterize the morphology of materials on length scales from 0.1 to 50 \( \mu \text{m} \). Some previously undetected morphological features can be
revealed with this technique. In this paper, the finely-ground powder was prepared by hand-grinding a piece of sample in a mortar and pestle to pass all material through a #625 mesh (i.e., an opening size of 20 µm), followed by putting samples in washers to test.

5.2.7. Scanning Electron Microscopy (SEM)

The surfaces of the materials were observed by field emission scanning electron microscopy (SEM) in an FEI Magellan 400 XHR-SEM (FEI Company, Hillsboro, OR, USA) at a low voltage of 5 keV beam voltage and appropriate beam current to avoid sample damage. The working distance is 4 mm. For the examined samples, it was not necessary to apply the conductive coating on the sample surface because the electron beam was generated at a low voltage and small current. Just a thin layer of powder samples needs to be stuck on the surface of the double-sided tape.

5.2.8. Water Contact Angle Measurements and Surface Energy

The water contact angles (WCAs) were measured in a Dataphysics OCA 15 EC contact angle measurement system. For the static WCA measurements, 10 µL water drops were used and static images were captured and analyzed. Each sample needs to be done for five different positions, and then calculate the average. Both powder and block samples were tested: while the block samples were cut and slightly polished to have a smooth surface, the powders were stuck on the double-sided tape on a glass slide and made sure that the surfaces have a flat and smooth surface for the WCA measurements. All measurements were performed at room temperature and atmospheric pressure. (Static WCAs are shown in Table 5.4).
Table 5. The water contact angle, DIM contact angle, and surface energy of each material

<table>
<thead>
<tr>
<th>Material</th>
<th>Water contact angle (°)</th>
<th>DIM contact angle (°)</th>
<th>Surface energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-AO</td>
<td>137.4 ± 0.3</td>
<td>126.3 ± 0.2</td>
<td>2.33</td>
</tr>
<tr>
<td>C-SHOP</td>
<td>162.6 ± 0.5</td>
<td>156.4 ± 0.4</td>
<td>0.091</td>
</tr>
<tr>
<td>C-Cyano</td>
<td>19.5 ± 0.4</td>
<td>11.3 ± 0.3</td>
<td>77.95</td>
</tr>
<tr>
<td>C-MK</td>
<td>40.3 ± 0.4</td>
<td>28.2 ± 0.5</td>
<td>66.32</td>
</tr>
</tbody>
</table>

The surface energy ($\gamma$) of all samples can be calculated with Fowkes Model. Fowkes’ surface energy theory was combined with the Young and Young-Dupree equations (Informática & Gitleman, 2014). This theory treats liquid and solid surface energy as polar and dispersive (nonpolar) components, and in this paper, water and diiodomethane were chosen as the test liquids (shown in Table 5.5).

$$\frac{\gamma_l (\cos \theta + 1)}{2} = \sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}$$  \hspace{1cm} (5.3)

where $\gamma_l^d$ and $\gamma_l^p$ are the liquid dispersive and polar components, respectively, and $\gamma_s^d$ and $\gamma_s^p$ are the solid dispersive and polar components, respectively.

Table 5.5 Polar and dispersive surface energy components of the test liquids (Kozbial et al., 2014)

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_l$ (mJ/m²)</th>
<th>$\gamma_l^p$ (mJ/m²)</th>
<th>$\gamma_l^d$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>72.8</td>
<td>51.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Diiodomethane (DIM)</td>
<td>50.8</td>
<td>0.0</td>
<td>50.8</td>
</tr>
</tbody>
</table>

The assumption is that the total surface energy is the sum of the dispersive and polar components as shown in Equation (5.4). The calculated surface energies of all materials are presented in Table 5.4.
\( \gamma_s = \gamma_s^d + \gamma_s^p \) 

(5.4)
5.3. RESULTS AND DISCUSSION

5.3.1. Surface Structures and Hierarchical Roughness

Figure 5.4 presents the surface structure from SEM for all materials at 1µm and 500 nm. The surface of metakaolin is almost flat and there are lots of layers stuck together, and just one or two levels can be observed on the surface (Figures 5.4g and 4h). However, Figures 5.4a to 4f indicate the surfaces of C-SHOIP, C-AO, and C-Cyano are rough and have hierarchical structures, but the surfaces are different based on the SEM images. C-AO material has lots of holes on the surface except for the hierarchical roughness (Figures 5.4a and 4b), which increases the total surface area. However, C-SHOIP and C-Cyano (Figures 5.4c to 4f) both have lots of bumps on the surfaces, which indicates the surfaces are hierarchical and also have more total surface area.

Based on the USAXS, the surfaces of the four materials are different (Figure 5.5). The surfaces of three materials, including C-AO, C-SHOIP, and C-Amino have three different levels, which are in accordance with the results of the SEM images. However, C-MK just has one level on the surface, which indicates the surface is almost flat and smooth.
5.3.2. Nitrogen Adsorption

According to the Brunauer-Deming-Deming-Teller (BDDT) adsorption isotherm classification, nitrogen adsorption isotherms of all materials can be classified as Type II, which presents that adsorption on these materials can be divided into three stages: monolayer adsorption, multilayer adsorption, and capillary condensation. The three stages are as follows: the adsorption isotherms of all materials have an inflection point at low relative humidity, (as shown in Figure 5.6), which means saturated adsorbed content in the monolayer adsorption regime. Before the low relative humidity, just monolayer adsorption can occur. When the relative humidity increases, the thickness of adsorbed layers stepwise increases, and then multilayer adsorption happens. With the
relative humidity reaching the initial capillary condensation pressure, the hysteresis loop can be formed based on the adsorption and desorption curves, which confirms that capillary condensation occurs in the process of nitrogen adsorbed on materials. Different materials have different pressures, the initial capillary condensation pressures of AO, SHOIP, Cyano, and MK are 0.36, 0.48, 0.56, and 0.84, respectively.

According to Equation (5.1), the specific surface area of each material can be calculated with the initial linear part of the plot in Figure 5.6 (Table 5.3). As shown in Figure 5.6, AO has the highest quantity adsorbed than the other three materials, which indicates AO has the largest SSA to make it has the best capacity to adsorb nitrogen. The sample MK takes up the least amount of absorbed nitrogen to the other samples over the entire range of RH values studied. That is because the surface of MK is smooth and the SSA is the smallest, but other materials have different hierarchical structures and roughness on the surfaces, which improve the capacity of adsorption.

For the above four pure materials, the pore diameter distributions of mesopores can be evaluated with BJH method from the adsorption branches. According to Figure 5.7, the pore in C-MK appears no specific peak, which means the pore size distribute well at the mesopore scale, and C-MK has a wider pore diameter distribution than other materials. However, the pores of the other materials are mainly focused on the region centered at 7.21 nm (for C-AO), 15.36 nm (for C-SHOIP), 12.09 nm (for C-Cyano) (Table 5.3). The results are in agreement with the results of SEM and USAXS, the three materials with hierarchical structures have larger SSA and smaller particle size than MK which has a flat surface.
Figure 5. 6 Nitrogen adsorption isotherm for all samples.

Figure 5. 7 Pore size distribution curves of all materials based on BJH method.
5.3.3. Unclean Materials for Water Vapor Adsorption

Based on Figure 5.8, for all unclean materials, the water retention curves are almost the same and the water contents are almost 50% at high RH, and the curves exhibit Type V isotherm according to the IUPAC (International Union of Pure and Applied Chemistry) classification. All the curves except for U-MK stepwise increase at the lower pressure, and the RH at about 44% is the first inflection point. Then the curves increase from 45% to 76%, and then gradually approach a stable except for SHOIP, and finally sharply increase from 76% to 90%. The curve of SHOIP has no stable stage until 90%. U-MK just adsorbed water vapor under high RH because there is no sodium hydroxide or sodium carbonate on the surface which will impact the adsorption. Therefore, according to Figure 5.8, it is hard to get any conclusion, or it is hard to tell the difference between hydrophilic and hydrophobic materials for isotherm adsorption. That is because the unclean materials have lots of sodium hydroxide, sodium bicarbonate, and sodium carbonate on the surfaces, all of them are water affinity or even react with water, which greatly impacts the behaviors of adsorption. For the isothermal adsorption of unclean materials, these remained materials adsorbed water vapor are dominant over the main materials. Therefore, it is hard to tell the difference between hydrophobic and hydrophilic materials with impurity stuff.

Figure 5. 8 Adsorption isotherm for unclean materials
5.3.4. The Clean Material for Water Vapor Adsorption

As mentioned above, clean materials mean that all materials are washed, so they are pure and without any other impurities. The isotherm curves for different materials present different types based on the IUPAC classification. There are two main types according to surface wettability: in the case of hydrophilic and superhydrophilic materials (C-MK and C-Cyano), the curves show Type II isotherms, and these samples have reduced isotherms which are convex toward the relative humidity axis in the highest range of pressures (Figure 5.9). For C-Cyano, the curve of adsorption increases at the lower RH, and the RH at about 40% is the first inflection point. Then the curve slightly increases from 40% to 80%, and then still increases from 80% with a larger slope and there is no stable stage even under high RH. There is adsorption hysteresis for both, and the adsorption hysteresis loops are closed, the shapes of hysteresis loops are often related to specific pore morphologies (Yurdakal et al., 2019). According to the isothermal adsorption and desorption curves of hydrophilic and superhydrophilic materials, there are also some differences: 1) the adsorption capacities are different, C-Cyano adsorbed much more than C-MK, which can be explained by not only C-Cyano is superhydrophilic materials but also the surface is much rough than C-MK; 2) C-Cyano as superhydrophilic material has several stages, such as increasing at lower RH, and then gradually approaching to a stable at medium RH, and finally continue increasing at high RH; 3) the adsorption curve of C-Cyano is still increasing at high RH, but the curve of metakaolin approaches to the stable at high RH; 4) C-Cyano has hierarchical adsorption, but C-MK just has the adsorption on the smooth surface because there are no multi-levels on the surface.

However, the curves indicate Type V for hydrophobic and superhydrophobic materials (C-AO and C-SHOIP), in some ways these curves tend to the sigmoid shape of the isotherms (Figure 5.10). From Figure 5.10, the adsorption curves are almost the same, they also have monolayer adsorption, multilayer adsorption, capillary adsorption, and hierarchical adsorption. The adsorption curve of C-SHOIP gradually increases with the relative humidity, and sharply increases from 84% to 88%, and finally approaches the stable stage. However, for C-AO, there is a little bit of difference because of a stable stage from 36% to 44%. In terms of adsorption capacity, C-AO adsorbed more water than C-SHOIP because the particle size of C-AO is smaller than the C-SHOIP and C-AO is less water-repellent than C-SHOIP, which leads to the SSA of C-AO being larger.
than C-SHOIP and C-AO can adsorb more water than C-SHOIP. Another obvious thing is the adsorption hysteresis loops are open for materials that are water-repellent, which are different with the shapes of hydrophilic materials. Therefore, the shapes of hysteresis loops are not only determined by the specific pore morphologies, but also related to the surface wettability.

Figure 5.11a presents the water adsorption change with relative humidity, but it can only tell the difference between hydrophilic and hydrophobic materials according to the shape of curves because it is hard to know which is hydrophilic or superhydrophilic based on the adsorbed water capacity. Therefore, according to Equation (5.2), Figure 5.11b shows the height change with relative humidity for all clean materials, C-Cyano as superhydrophilic material does have a thicker layer of water than other materials at most of the relative humidity, but it is still hard to tell the difference.

However, combined with the SSA, pore size, and surface morphology, there is an interesting thing: the smaller the pore diameter the more adsorbed capacity. AO is 7.21 nm, so the adsorbed water capacity is the best (as shown in Figure 5.11a). Therefore, the adsorbed capacity for hydrophilic and hydrophobic materials is not only related to the surface wettability but also is dependent on the surface roughness, like hierarchical surface, SSA, and particle size. It is reasonable to consider the difference in the thickness of adsorbed water which is calculated with Equation (5.2). The C-Cyano has the largest thickness adsorbed water at the monolayer adsorption, but for multi-layer adsorption, the thickness is not the largest because the hierarchical surface is the main reason to influence the adsorption, which is not only determined by surface wettability but also determined by the surface roughness. That can explain why C-MK is even a hydrophilic material, but the thickness is the thinnest, that because the surface of C-MK is smooth, the particle size is much larger than other materials, and the specific surface area is smaller than other materials. However, at high RH (almost 90% RH), C-Cyano still has the thickest film of adsorbed water because of the surface wettability, it can still adsorb more water than other materials which achieve the saturated condition.
Figure 5. 9 Isothermal adsorption curves for hydrophilic materials: (a) isothermal adsorption and desorption curves for C-Cyano (superhydrophilic material); (b) isothermal adsorption and desorption curves for C-MK (hydrophilic material).

Figure 5. 10 Isothermal adsorption curves for hydrophobic materials: (a) isothermal adsorption and desorption curves for C-SHOIP (superhydrophobic material); (b) isothermal adsorption and desorption curves for C-AO (hydrophobic material).
5.3.5. The Rate of Adsorption

The rate of adsorption somehow indicates the properties of the sorbent. Figure 5.12 presents the adsorption rate at different RH (97%, 55%, 11%, and 6%). At RH= 97%, the C-MK in Figure 5.12a is almost linear without increasing and decreasing after one day, because the surface of C-MK is smooth, when finished the adsorption, there is no space for extra water to adsorb. However, the other three materials have several stages, all of them increase at the beginning, which is the monolayer adsorption, then approach a stable stage for one or two days, and increase again with continuous time, which is the multi-layer adsorption or capillary adsorption. The reason is that the three materials have hierarchical structures and roughness, so there are more spaces for water to adsorb after finishing the previous stage.

Figure 5.12b presents RH as 55%, C-MK has little water adsorbed with time from the curve. The other three materials have the same almost rate of adsorption: sharply increasing in the first three days for monolayer adsorption, then gradually increasing for two days, and finally approaching the stable stage with time.

At RH= 11%, C-MK has no adsorption at the beginning time (Figure 5.12c), because there is not enough water vapor to adsorb when the relative humidity is very low, but there is a little bit of adsorption after eight days, and then tends to the stable stage. The other three materials have
the same shape of curves: slightly increasing at the initial stage, then approaching a stable stage, and sharply increasing at the final stage. At the initial stage, C-AO is a little bit more adsorbed water than the other two materials, which is monolayer adsorption, but at the final stage, C-Cyano has more adsorbed water than the other two materials, which means the surface wettability domain in this stage.

At RH=6%, C-MK has no adsorption at the first three days and then starts to adsorb and finally approaches stable (Figure 5.12d). The other three materials have the almost same shape of curves: there is an increase in the first two days, then keep the adsorbed water for one day, and increases a lot on the fourth day, there is a little bit of a decrease after hugely increasing, and finally approach to the stable. It is easy to notice surface wettability influences the adsorption much more than surface roughness under low pressure. As shown in Figures 5.11 c and d, the C-Cyano has the highest adsorption than other materials.

The obvious difference is that the hierarchical structure helps the surfaces of materials adsorb more water than the smooth surface so that C-MK adsorbs the least water, and the rate of adsorption is the lowest, especially at the lower RH, there is no adsorbed water for C-MK at the first several days. At the highest RH, the adsorption rate of C-AO is the highest, and the adsorbed water is the most, that is because C-AO has the largest SSA and smallest pore diameter, so surface roughness impact more than surface wettability under high pressure. However, C-Cyano has the highest adsorption rate and adsorbs the most water at the lower RH, therefore, surface wettability influences much more than surface roughness during low RH. C-AO has the largest SSA and smallest particle size, the hierarchical structure domains at high RH because water vapor is enough to adsorb, but at lower RH, the water vapor is not enough, and the surface wettability is more important than roughness.
Figure 5. The rate of isothermal adsorption: (a) the rate of isothermal adsorption at RH= 97%; (b) the rate of isothermal adsorption at RH= 55%; (c) the rate of isothermal adsorption at RH= 11%; (d) the rate of isothermal adsorption at RH= 6%.

5.3.6. The Models

For monolayer adsorption on clay minerals, the widely used BET adsorption model is suitable to fit the experimental water adsorption isotherms, especially for the lower pressure (0.05-0.35 $P/P_0$), where monolayer adsorption can happen (Bardestani et al., 2019). According to the BET theory assumption, the adsorption energy is not related to the adsorption sites, and gas molecules interaction just occurs in the vertical direction, so the lateral interactions between
adjacent adsorbed molecules can be neglected (Q. Chen et al., 2017). Physical adsorption of the first layer is as follows:

\[ V = \frac{V_m \times C \times R}{(1-R)(1+C \times R - R)} \]  

(5.5)

where, \( V \) is the mass adsorbed at relative humidity; \( V_m \) is the required mass of adsorbate consisting of a complete monolayer adsorbed on the sample; \( C \) is a constant, which means the differences in the heat of adsorption of the first and higher layers, and depend on temperature and on the heat of adsorption of the initial layer; \( R \) is the relative humidity \( (R = P/P_0, P \) and \( P_0 \) are the actual and saturated vapor pressures of adsorbate).

At the lower pressure \( (\text{RH} \leq 0.35) \), the BET model can be applied for C-AO, C-SHOIP, and C-Cyano samples (as Table 5.6), and the value of \( R^2 \) is almost 0.99. The maximum required mass of adsorbate \( V_m \) is C-Cyano, which that indicates the hydrophilic or superhydrophilic material can adsorb much more than hydrophobic or superhydrophobic material for monolayer adsorbed. These results also can be confirmed with the rate of isothermal adsorption at low RH (Figure 5.12 d).

BET model offers information on monolayer adsorption on external surfaces at low RH values, but it could not indicate adsorption on heterogeneous surfaces at high RH values. Thus, it is necessary to find other models to fit the experimental data. The Freundlich is another widely used isotherm model in adsorption, which is used to represent the nonlinear adsorption phenomenon (Al-Ghouti & Da’ana, 2020b). The linear and nonlinear equations of the Freundlich model are as follows:

\[ \log V = \log a + \frac{1}{n} \log R \]  

(5.6)

\[ V = a \times R^{1/n} \]  

(5.7)

where \( a \) and \( n \) are constants, the Freundlich model will reduce to the linear model when \( n = 1 \).

The Freundlich model is normally treated as an empirical equation without physical meaning. But for multi-layer adsorption on heterogenous surfaces, the Freundlich extension is more appropriate.

\[ V = a \times R^{b \times R^{-c}} \]  

(5.8)
where $a$, $b$ and $c$ are constants.

Table 5. Isotherm constants for each model.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>BET model</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
<th>vG model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{C}=25.783$</td>
<td>$a=0.599$</td>
<td></td>
</tr>
<tr>
<td>C-Cyano</td>
<td>$V_m=0.149$</td>
<td>$b=4.132$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9951$</td>
<td>$c = -1.426$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9852$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 1765.724$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-MK</td>
<td>N/A</td>
<td>N/A</td>
<td>$b = -1492.855$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$c = 1.735$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R^2 = 0.8912$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C = 11.641$</td>
<td>$a = 0.134$</td>
<td>$a = -5.595$</td>
</tr>
<tr>
<td>C-SHOIP</td>
<td>$V_m = 0.038$</td>
<td>$b = 2.295$</td>
<td>N/A</td>
<td>$n = 5.587$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9946$</td>
<td>$c = -0.835$</td>
<td></td>
<td>$R^2 = 0.9882$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9905$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C = 7.160$</td>
<td>$a = 0.122$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-AO</td>
<td>$V_m = 0.034$</td>
<td>$b = 3.187$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9918$</td>
<td>$c = -1.018$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.9915$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Freundlich model is suitable for surfaces that are heterogeneous and hierarchical, so the model can be applied for C-AO, C-SHOIP, and C-Cyano materials, and the values of $R^2$ are almost 0.99. From the results of Table 5.6, the values of $\frac{1}{n}$ can be calculated by combining the Equation (5.7) with Equation (5.8) (Figure 5.14). $1/n$ is the potency of the adsorption or means the surface is heterogeneous which indicates the energy relative distribution and the heterogeneity of the adsorbate sites. The value of $1/n$ for C-Cyano is larger than the other two materials because of the surface wettability. The SSA of C-AO is larger than C-SHOIP, so the value of $1/n$ for C-AO is much larger than C-SHOIP.
Langmuir isotherm model assumes the thickness of the adsorbed layer is monolayer adsorption in which adsorption process takes place at identical and equivalent definite localized sites. The adsorption process is based on a kinetic principle in which a continuous bombardment process of molecules onto the surface with corresponding molecules’ desorption or evaporation from the surface with no accumulation at the surface. There are no steric hinderance and lateral interaction, even on adjacent sites, between the adsorbed molecules. The extended Langmuir isotherm model is presented as Equation (5.9).

\[ V = \frac{1}{a + b \cdot R^{c-1}} \]  

where, \( a \), \( b \), and \( c \) are constants.

Based on the assumptions of the model, C-MK has a smooth surface, the rates of adsorption and desorption are the same (Figure 5.9b), so it is suitable for simulation with the model, and the \( R^2 \) is 0.8912.

vG model is more complexed than the above model, but it can produce a continuous output in the unsaturated area and provide a good description of the soil-water characteristic curve under
most circumstances (Revil & Lu, 2013)(Rajesh & Khan, 2018). The equation for isothermal adsorption as follows (Rajesh & Khan, 2018):

\[
V = 0.02 + \frac{0.11}{\left[1 + (a \cdot l \cdot nR)^n\right]^m}
\]  \hspace{1cm} (5.10)

where, \(a\), \(n\), and \(m\) are constants \((m = 1 - \frac{1}{n})\).

C-SHOIP is a complicated material for isothermal adsorption, because not only the material is superhydrophobic, but also it has a high-hierarchical structure, so for high pressure, vG model is the best model to simulate, and the \(R^2\) is 0.9882.

5.4. CONCLUSIONS

Alkali-activated method for different materials with functional groups synthesize two different surface wettability. The isotherm adsorption behaviors and curves for hydrophilic and hydrophobic are different. It is hard to tell the difference based on the adsorption capacity, because for hydrophilic and hydrophobic materials, the adsorbed capacity is not only related to the surface wettability, but also is dependent on the surface hierarchical (SSA and particle size). At high RH or multilayer adsorption, surface hierarchical plays more important role, the smaller particle size, the more adsorbed water vapor. However, at low RH or monolayer adsorption, the surface wettability is the more important. However, for smooth surface materials, hydrophilic and hydrophobic materials can be told with the curves and adsorption mechanisms. Especially, the isotherm curves of hydrophilic materials present Type II, but the curves of hydrophobic materials show Type V.

In order to tell hydrophilic and hydrophobic materials, it is not easy to use the quantity of adsorbed water to make the difference, even it is wrong. It should be combined with the thickness of the water film, the size of pore, SSA, the surface morphology, and the rate of adsorption at certain range of RH.

At the lower pressure (\(RH \leq 0.35\)), the BET model can be applied for materials with hierarchical surface structure, and the value of \(R^2\) is almost 0.99. When the RH \(\geq 0.35\), the FreundlichEXT model is much more suitable for the materials with rough surface. Based on the
values of $\frac{1}{n}$, C-Cyano has the more capacity to adsorb more water than other two materials. For C-SHOIP, vG model is applied to describe the adsorption when RH > 0.82 because of the surface wettability and morphology. For smooth surface, like C-MK, LangmuirEXT is enough to describe all the range of RH, and the $R^2$ is 0.8912.
6. SURFACE MODIFICATION FOR SAND AND CLAY WITH 
DIMETHYLDICHLOROSILANE

Modified surface with alkyl groups can alter the surface wettability of materials, even with short chain organosilanes (dimethyldichlorosilane). There are two conditions to modify: (1) in the vapor phase; (2) in the liquid phase. It is obviously noticed that modified materials under the vapor phase have higher water contact angles because the oligomeric layers produced in the vapor phase shields the polar surface. The modified materials show hydrophobic properties because the surface is covered with -CH₃ groups which confirmed with Fourier transform infrared spectroscopy. The largest water contact angle is 146.9 ± 0.5°, the breakthrough pressure is almost 50 kPa, and the lowest permeability is 1.39 ×10⁻⁶ m/s. Therefore, the hydrophobized clay and soils can be used as the barrier to prevent water flow and other fields. In addition, there are two factors to influence the hydrophobic property of modified materials under same conditions: the first one is the surface roughness of the untreated material, the rougher material has, the higher the water contact angle; the other one is the pore diameter, the smaller size of pore diameter, the higher water contact angle.
6.1. INTRODUCTION

The water-repellent soil was induced by wildfire, and the soil was found it is a good way to alter the hydrological response, and it can be applied to restrict soil water movement and redistribution, lower infiltration rate, and promote surface runoff to keep the stability of a slope (Debano, 2000; Doerr, 1998; Ritsema & Dekker, 2000). Lots of experiments reveal the decreasing of saturated hydraulic conductivity on water-repellent soils. Other soil properties can be influenced by water repellency, such as water retention, water drop impact, permeability, and friction angle. Therefore, soil wettability is a measure of the affinity of soils for water, and it determines the behaviors and properties of soils (Tohari et al., 2007). Hydrophilic soils are an affinity for water, and the infiltration rate is very high, and rainwater can penetrate through and flow away, which induces a rapid increase in the pore water pressure and lowers the effective stress, therefore, the soil strength would be eventually impacted or failed. The other influence is that hydrophilic soils are easy to form a saturated zone, which will impact the slope stability (Ebel et al., 2012). However, hydrophobized soils can reduce the infiltration rate and improve the erodibility which results in enhanced overland flow and erosion.

Even though water-repellent soils have lots of advantages for the engineering field, it is still challenging to achieve soil with the hydrophobic or superhydrophobic properties. Synthesize of water-repellent soils had been used to harvest water in arid areas (S. Zheng et al., 2017). Water-repellent soils were used as a layer to prevent water penetration and protect the pavement base (Jordaan & Steyn, 2021). The normal method to achieve hydrophobized soils is to modify the surface of materials.

The surface modification of micro-particles includes chemical treatments, grafting of (Fadeev & McCarthy, 2000) coupling agents were published by Plueddemann, and then modification nanoparticles with silane coupling agents were widely used to improve the compatibility between the particles and polymer surfaces and the properties of composite materials (Y. Guo et al., 2008; Lung & Matinlinna, 2012). The material can be modified with some functional groups, such as silica can be modified with organosilanes, which makes silica with -CH₃ groups and has hydrophobic properties (Z. Bai & Zhang, 2020; Fadeev & McCarthy, 2000).
A nanoparticle modified with a 3-methacryloxypropyl trimethoxysilane coupling agent leads to the nanoparticle dispersing well in organic solvents. Methacryloxypro-pyltrimethoxysilane (MPS) was used to modify the surface of silica, which indicates the grafting ratio of MPS on the surface of nanoparticles increased with the MPS content (Y. Guo et al., 2008).

The grafting of synthetic polymers is the method to modify the surfaces of organic or inorganic materials by grafting synthetic polymers to the surface of the substrates (Z. Bai & Zhang, 2020). It can strengthen the chemical functionality and change the surface roughness of materials (Prucker & Rühe, 1998). There are two ways to graft polymer chains on the surface of materials: the first one is the functional groups that react with the surface of materials; the other one grafting from the self-assembled procedures (Mansky et al., 1997; Tran & Auroy, 2001). To improve the interfacial interaction in alumina nanoparticles filled polymer composites, grafting polystyrene and polyacrylamide on the surface of particles was used to alter the surface characteristics (Rong et al., 2002). PMMA chains were directly grafted from the surface of the TiO₂ nanoparticles in water to improve the thermal stabilities and have a high melting temperature (X. Wang et al., 2007). Grafting vinyl polymers on the surface of polymericsiloxane was used to induce the hydroxyl groups on the surface of TiO₂ (Rong et al., 2002).

Another method is the ligand exchange technique. Removing the surface ligand provides more space for charge separation by decreasing the distance between NPs and between NP-polymer contacts to lessen recombination losses and improve charge transport (Greenham et al., 1996; Murray et al., 1993). High-quality NPs can be prepared in the presence of capping ligands under a sufficiently high temperature, and the size can be determined by stopping the reaction at different growth stages or by altering the ligand concentrations (Z. Lu & Yin, 2012).

In this paper, combined with changing the surface wettability of soils, chemical treatment is used to modify the surface of clay and sands. Hydrophobized clay and sands are prepared under two different conditions: in liquid and vapor phases. The hydrophobized clay and sands are investigated to study the difference under different conditions and the impact factors under same conditions.
6.2. MATERIALS AND METHODS

6.2.1 Materials

The as-received dry powder of PowerPozz™ metakaolin (MK, ≤16.2 nm, SiO$_2$-Al$_2$O$_3$, Table 3.1) was chosen from Advanced Cement Technologies, LLC., WA, USA. Glass beads (acid-washed, 150-212 µm) were purchased from Sigma Aldrich Co., MO, USA. Ottawa sand (≤150 µm, model No. HM-106) came from Gilson Company, Inc., USA. Ammonium hydroxide (NH$_4$OH), hydrogen peroxide (30%, H$_2$O$_2$), and sulfuric acid (98%, H$_2$SO$_4$) were used as received from Fisher Scientific, Inc., USA. Ethanol is HPLC grade and was purchased from Fisher Scientific, Inc., USA. Dimethyldichlorosilane (DMDCS, C$_2$H$_6$Cl$_2$Si, 99+) was chosen from Acros Organics, Inc., NJ, USA.

6.2.2 Surface Modification with Dimethyldichlorosilane (DMDCS)

The procedure started with cleaning the surface of the materials (Figure 6.1). MK, Ottawa sand, or glass beads were put into the solution of ammonium hydroxide, hydrogen peroxide, and deionized water with a ratio of 4:1:1, and the material should be immersed in the solution for 15 min. Rinsed the material with copious amounts of water and dried the material after rinsing. Put the material into the mixture of concentrated sulfuric acid and hydrogen peroxide with a ratio of 7:3 after drying, and still the material needed to be immersed in the solution and stayed in the mixture overnight. Rinsed again the material with enough water after submersion and immediately dried the material in a clean oven at 120°C for 24 hours.

In this paper, to investigate the difference between the two methods, there are two ways including the liquid phase and vapor phase to modify the surfaces of the powders. The vapor phase method: the dried powder material was placed in an aluminum weighing dish, and the dish was put into a glass jar. A small tube containing 5 mL of organosilane reagent (DMDCS) was also put into the glass jar. Then put the sealed glass jar into a clean oven at 70°C. The powder material was not in contact with the liquid silanes, the vapor-phase reaction took place for three days, and to make sure the powder material can adsorb the vapor of DMDCS, it is necessary to stir the powder up-down every day. The hydrophobized material was then rinsed with ethanol three times, ethanol
and water with a ratio of 1:1 for two times, water for two times, ethanol for two times, and then water for the last three times. Finally, immediately put the rinsed material into a clean oven at 120°C for 24 hours. The surface modifications of samples are designated as “MMK”, “MOS”, and “MGB” hereafter for MK, Ottawa sand, and glass beads, respectively.

The liquid phase method: the procedures are almost the same with the vapor method, just one difference is the powders are directly mixed with the DMDCS (Figure 6.1). The dried powders needed to cool to room temperature first and then were put into a flask containing DMDCS solution (5 mL). The reaction mixtures were held at 70°C for 3 days so the DMDCS treatments would be chemically stable and inert. Then the powders were rinsed and handled as described above for cleaning the surface. The surface modifications of samples in liquid are designated as “LMMK”, “LMOS”, and “LMGB” hereafter for MK, Ottawa sand, and glass beads, respectively.

Figure 6.1 The procedures to modify the surface of materials.
6.2.3. Methods

6.2.3.1. Water Contact Angle (WCA) and Surface Energy

Water contact angle (WCA) was measured by the Ramé-Hart Model 210 telescopic goniometer and a syringe with a 24-gauge flat-tipped needle at room temperature. The procedure to measure contact angles for powder samples is different from solid samples, which includes attaching a double-sided adhesive tape to a glass slide and adding the powder samples onto the tape evenly, after that, filtered pressurized air was used to remove the extra powders. The volume of a water droplet for WCA measurement was 10 μL of deionized water. Five different areas of the sample surface were measured with the sessile drop method and then calculated the averages of the WCA (shown in Table 6.2).

The surface energy ($\gamma$) of our samples can be calculated with Fowkes Model. Fowkes’ surface energy theory was combined with the Young and Young-Dupree equations (Informática & Gitleman, 2014). This theory treats liquid and solid surface energy as polar and dispersive (nonpolar) components, and in this paper, water and diiodomethane were chosen as the test liquids (shown in Table 6.1).

$$\frac{\gamma_l (\cos \theta + 1)}{2} = \sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p} \quad (6.1)$$

where $\gamma_l^d$ and $\gamma_l^p$ are the liquid dispersive and polar components, respectively, and $\gamma_s^d$ and $\gamma_s^p$ are the solid dispersive and polar components, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_l$ (mJ/m$^2$)</th>
<th>$\gamma_l^p$ (mJ/m$^2$)</th>
<th>$\gamma_l^d$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>72.8</td>
<td>51.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Diiodomethane (DIM)</td>
<td>50.8</td>
<td>0.0</td>
<td>50.8</td>
</tr>
</tbody>
</table>

The assumption is that the total surface energy is the sum of the dispersive and polar components as shown in Equation (6.2).
\[ \gamma_s = \gamma_s^d + \gamma_s^p \] (6.2)

The calculated surface energies of carbon-based reinforcements of superhydrophobic polymers are presented in Table 6.2.

### 6.2.3.2 Breakthrough Pressure

The breakthrough pressure is the pressure to force water to penetrate through the hydrophobic materials. It was tested with the equipment that was built-up on our own (Figure 6.2). The inner surface of the syringe was coated with a thin layer of the grease to prevent leakage between hydrophobic/superhydrophobic material and the interior wall of the syringe. The holes (Figure 6.2a) were created on the bottom to make sure the water can flow away after breakthrough. The compaction stress to compress the powder sample (Figure 6.2c), and connect the given water pressure with the syringe, in which the rate of water pressure is 0.5 kPa/s.

Figure 6.2 The set-up for breakthrough pressure: (a) the syringe with holes; (b) the set-up to inject water pressure; (c) compaction powder in the syringe.
6.2.3.3 Water Penetration

About 10g powder sample in weighing bottles with 23.5 mm in inner diameter and 17 cm in height were used to measure the time of water flow through the powder samples under natural condition without. Some deionized water was added into the bottles, and make sure enough water can penetrate through the samples. Record the time and the weight of flow out water. The time taken for the complete penetration of the water was measured with a stopwatch. Then the permeability can be calculated from five replicates.

6.2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

To achieve the infrared spectrums of powder samples, Fourier transform infrared spectroscopy (FTIR, IR Tracer-100 FT-IT spectrometer, Shimadzu Corp., Kyoto, Japan) was used to analysis the samples. The system has very high excellent sensitivity with an SN ratio of 60,000:1, a high resolution is at 0.25 cm\(^{-1}\), and the high speed scanning capability is 20 spectra/second. In this paper, the IR spectra in the range of 4000-600 cm\(^{-1}\).

6.3. RESULTS AND DISCUSSION

6.3.1. Water Contact Angle and Surface Energy

Water contact angles and surface energies can be calculated based on the above (Table 6.2). All contact angles are greater than 90º, which indicates these materials are hydrophobic materials (Figure 6.3). The table also includes the water contact angle of SHOIP (superhydrophobic hybrid organic-inorganic polymer) which mentioned in the previous chapter, this material was synthesized with another method, and it is a superhydrophobic material, and further information of SHOIP is out of the focus of this chapter. From the table, it is observed that the water contact angles of modification from vapor phase are higher than the modification from liquid phase, and the water contact angle of SHOIP is the highest. Under the same conditions, the water contact angle of modified MK is larger than OS and GB, in fact, modified GB has the lowest contact angle. The surface energy of SHOIP is the lowest, but the surface energy of LMGB is the highest, which
confirms the higher surface energy, the lower WCA. Due to the modification from vapor phase has higher water contact angle, so further discussion is focused on materials modified with vapor DMDCS in this paper.

Table 6. 2 Water contact angle and surface energy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Water Contact Angle (°)</th>
<th>Diiodomethane Contact Angle (°)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHOIP</td>
<td>162.6 ± 0.5</td>
<td>156.4 ± 0.4</td>
<td>0.091</td>
</tr>
<tr>
<td>MMK</td>
<td>146.9 ± 0.5</td>
<td>132.6 ± 0.5</td>
<td>1.332</td>
</tr>
<tr>
<td>MOS</td>
<td>111.6 ± 0.3</td>
<td>97.3 ± 0.5</td>
<td>11.086</td>
</tr>
<tr>
<td>MGB</td>
<td>101.3 ± 0.5</td>
<td>90.4 ± 0.4</td>
<td>15.708</td>
</tr>
<tr>
<td>LMMK</td>
<td>134.5 ± 0.3</td>
<td>122.4 ± 0.4</td>
<td>2.932</td>
</tr>
<tr>
<td>LMOS</td>
<td>102.3 ± 0.4</td>
<td>90.5 ± 0.3</td>
<td>15.375</td>
</tr>
<tr>
<td>LMGB</td>
<td>92.4 ± 0.3</td>
<td>83.3 ± 0.4</td>
<td>21.043</td>
</tr>
</tbody>
</table>
The water contact angles for all modified materials: (a) the WCA for MMK; (b) the WCA for MOS; (c) the WCA for MGB; (d) the WCA for LMMK; (e) the WCA for LMOS; (f) the WCA for LMGB.

6.3.2. FTIR Results

Figure 6.4 presents the FTIR spectrums for materials modified with DMDCS in vapor phase. All three modified materials under vapor phase show C-H stretching at 1450 cm\(^{-1}\) from methyl group, which indicates the three materials have hydrophobic property. The characteristic peaks for pure MK were observed at 667, 797, and 1093 cm\(^{-1}\) owing to Si-O-Si symmetric stretching, Al-O-Si stretching, and Si-O-Si/Si-O-Al stretching, respectively. There are some obvious different peaks between the untreated MK (pure MK) and treated MK (MMK) in Figure 6.4b: the peak around 1450 cm\(^{-1}\) was assigned to the C-H bending, which comes from the methyl group and contributes to the water-repellent, and the range between 2800-3300 cm\(^{-1}\) indicates there are O-H stretching, which comes from the alkaline treatment for surface, and there are still some remained -OH which did not react with DMDCS.
Figure 6.4 The FTIR spectrums: (a) the FTIR spectrums for modified GB, OS, and MK; (b) the FTIR spectrums for untreated MK and modified MK.
The WCA of SHOIP is larger than 150°, and the WCA of MMK is almost 150°, but these two materials were synthesized with two different organosilanes. Therefore, to compare the difference, Figure 6.5 shows the spectrums for SHOIP and MMK. There are adsorption bands at 1450 cm\(^{-1}\) for both materials, which indicates there are -CH\(_3\) groups on the surface. SHOIP has the adsorption bonds at 862 and 991 cm\(^{-1}\), because the main synthesized material includes metakaolin, so it has Si-O-Si or Si-O-Al stretching. In fact, the MMK also has the Si-O-Si and Si-O-Al stretching as discussed before. The difference is O-H bending at the range between 3000 and 3647 cm\(^{-1}\) observed on the spectrum of SHOIP, that is because the synthesized procedure includes hydrolysis and condensation reaction, so there are -OH groups. However, the MMK also has the -OH groups at range of 2800-3300 cm\(^{-1}\), which come from the alkaline treatment for the surface of MK.

Figure 6. 5 The FTIR spectrums for SHOIP and modified MK (MMK).
6.3.3. Breakthrough Pressure and Permeability

Figure 6.6 shows the breakthrough pressure for MMK, and the pressure is almost 50 kPa. For breakthrough pressure, there are no pressures for MOS and MGB, because the pore diameters are too large, and the water is easy to penetrate through the voids, so it is hard to measure the pressure before the water through the voids among the powders.

![Graph showing breakthrough pressure for MMK](image)

Figure 6.6 Breakthrough pressure for MMK.

For the materials with large pore diameters, the water penetration was used to measure the permeability of materials under natural condition without any compaction (Table 6.3). According to Table 6.3, the permeability of MOS is smaller than MGB’s because the pore diameter of OS is smaller than GB and also MOS is more water-repellent than MGB due to the surface morphology. When they were under natural condition without compaction, the voids of OS are also smaller than GB, and the surface of MOS repels water more than MGB, so the water is harder to penetrate MOS and the $k$ of MOS is smaller.
Table 6.3 The permeability of materials

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Permeability, k (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGB</td>
<td>$4.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>MOS</td>
<td>$1.39 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

6.4. DISUSSION

According to Figure 4.14e, the surface of SHOIP has lots of -CH$_3$ groups which contribute to it has superhydrophobic property. Compared with the surface of MMK, it also has lots of -CH$_3$ groups, but MMK just presents hydrophobic property. That is because the surface of MMK also has lots of -OH groups, some of them are under the shield of the oligomeric layers, but there are still others are exposed on the surface, which attributes to affinity to the water, so the water contact angle of MMK is smaller than the SHOIP’s. Based on the water contact angles and surface energies for MK, OS, and GB, the vapor phase method yields surface with higher contact angle and lower surface energy. That is because DMDCS in the vapor phase produce oligomeric layers that shield the polar surface (as shown in Figure 6.7a), but the reaction in the solution phase yields monolayers that have accessible silanol groups which contributes to affinity to the water (Figure 6.7b). Therefore, the WCAs of materials modified under liquid phase are lower than materials modified under vapor phase.

In addition, the water contact angle of SHOIP is highest in the Table 6.2, that because the surface of SHOIP is covered with -CH$_3$ groups after hydrolysis and condensation, but the surface of materials modified with DMDCS has -CH$_3$ groups, and has some other groups, like -OH which contributes to affinity to water. Even under the same condition, like modified with vapor-phase, the water contact angle of MMK is higher than MOS and MGB, and the water contact angle of MOS is higher than MGB, that is the pore diameter of metakaolin is the smallest, and the pore diameter of GB is the largest. The larger pore diameter, the lower water contact angle. Meanwhile, the surface of untreated OS is rough, but the surface of untreated GB is smooth, which leads the rough surface of MOS contributes it has higher contact angle than MGB.
The hydrophobic property can be indicated with FTIR results, each modified material has -CH\(_3\) groups. However, when compared with superhydrophobic (SHOIP), even all still have -CH\(_3\) groups, but the contact angles are different. The main reason is SHOIP was synthesized with hydrolysis and condensation procedures, and the surface is filled with -CH\(_3\) groups, but MMK came from the grafted. From the synthesize procedures, it is known that the surface of metakaolin needs to be treated under alkaline condition to make the surface with -OH groups. When reacted with DMDCS, the surface with -OH groups can react with DMDCS, so the surface of clay or sand can be grafted with organosilane. In addition, there are still some -OH groups remained on the surface of MMK. The clay or sand should be always kept dry, that is because Si-Cl bonds are easy under hydrolysis to form Si-OH groups when exposed to the ambient atmosphere.

6.5. CONCLUSIONS

Chemical surface modification induces the -CH\(_3\) groups on the surface of materials, which leads to the modified materials have hydrophobic property. The modified materials under vapor condition have higher water contact angles than under liquid phase that because synthesis under vapor phase produce oligomeric layers that shield the polar surface, but the reaction in the solution phase yields monolayers that have accessible silanol groups which contributes to affinity to the water. When the surface of untreated material is rougher, the higher water contact angle can be achieved. In addition, the pore diameter of untreated sample is another factor to influence the
hydrophobic property: the smaller size of pore diameter, the higher contact angle will be. The breakthrough pressure is high as 50 kPa for MMK, which contributes to modified MK can be applied to geotechnical engineering or practical applications. The permeability of MOS is smaller than MGB that because the surface of OS is rougher than the surface of GB, and the particle diameter of OS is smaller than GB. The hydrophobic clay and sand are promising materials to be used in engineering field.
7. CONCLUSION AND FUTURE WORK

7.1 CONCLUSIONS

The overall objective of this dissertation was to understand the mechanisms of reinforcements for carbon-based nanomaterials combined with geopolymer, study the influence of ultrasonic waves, temperature, and viscosity on the distribution of graphene in the vertical direction at micro/macro scale, distinguish the difference of isothermal adsorption between hydrophilic and hydrophobic materials, and modify the surfaces of clay and sand with functional groups. In this section, a summary of the major findings obtained through all experimental studies on the reinforcements of carbon-based nanomaterials, the impact factors on the distribution of graphene and isothermal adsorption, and surface modification for clay and sand is presented as follows:

- The carbon-based nanomaterials are promising materials to improve the strength of the composite, and each of them has the same and different mechanisms, which are related to their own chemical and physical structures.
- Ultrasonic waves not only break the bond of C=C to make carbon-based nanomaterials physically tangled with the aluminosilicones, but also helps the nanoparticles disperse well in the slurry.
- Ultrasonic waves not only greatly help improve the strength of the composite, but also can affect the dispersity of graphene. However, the ultrasonic wave is not the main way to control the dispersion when compared with temperature. The viscosity has no significant influence on the distribution of graphene at both micro/macro scale in the vertical direction, but less amount of water can modestly increase the strength of the composite.
- The isotherm curves for hydrophilic and hydrophobic materials are different, and the quantity of adsorbed water was not only determined by the surface wettability, but also controlled by the size of pore diameter, SSA, and the surface morphology of materials.
• The modified materials under vapor condition have higher water contact angle than under liquid phase, and the surface modification with functional groups is a good way to change the surface wettability of materials. The surface morphology and the size of pore diameter are very important factors to influence the surface wettability.

7.2 FUTURE PROSPECTIVES

Even though the new findings obtained from this dissertation, there are still some potential research topics that can be explored in the future, which are briefly described as follows:

(1) Measuring the three parts (such as top, middle, and bottom parts) for carbon-based nanomaterials to study the distribution and dispersion of other carbon-based nanoparticles in vertical direction.

(2) Quantifying the amount of graphene for each layer, like thermogravimetric analysis (TGA) can be used to measure the massing loss of carbon when the temperature is up to 1000°C.

(3) Cavitation induced by high temperature when cured the slurry was assumed in this dissertation based on observations and experiences, but the better way is to record the phenomenon or bubbles when preparing the slurry.

(4) Exploring the application of modified materials into the geotechnical engineering and more fields, such as pavement, protection of slope stability, and water harvesting in the arid regions.
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